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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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TECHNICAL PROGRESS REVIEWS

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

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ARGONNE NATIONAL LABORATORY

SPRING 1965

VOLUME 8

NUMBER 2

Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significantly new results have been obtained. The Review does not purport to abstract all the literature published in this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

The Eurochemic Processing Plant at Mol, Belgium

A first installment of a general description of the Eurochemic (European Company for the Chemical Processing of Irradiated Fuels) installation at Mol, Belgium, is presented in Ref. 1. Eurochemic, an international shareholding company, was created in July 1959 under the auspices of the European Nuclear Energy Agency by its 13 member countries. The purpose of the company is to process fuel elements used in atomic reactors to extract plutonium produced during irradiation and to recover uranium. Reference 1, which is reviewed in more detail in Sec. II of this issue of *Reactor Fuel Processing*, describes the general plant layout and the facilities for fuel reception, fuel handling, processing, safety and analytical control, and storage of the final product. Completion and testing of the plant will take place this year. (Earlier reviews of the scope and initial economic aspects of the Eurochemic plant were given in previous issues of this journal.[2–5])

Processing by the U. K. Atomic Energy Authority

A 1964 Geneva Conference paper (Ref. 6) discusses the design and development of the new British nuclear fuel-processing plant at Windscale, which provides additional capacity to the first separation plant at Windscale. The additional capacity is needed for continuing the U. K. nuclear power program initiated in 1955, which is based on the Calder Hall type of reactor. This type of reactor is fueled with natural uranium clad in Magnox, a magnesium alloy. This program is to be the first phase of a balanced power system of thermal and fast reactors, in which plutonium from the first generation of Magnox reactors is to be used in the fast reactors.

The new plant, a centralized unit designed for economical continuous operation, will yield highly decontaminated products. The yearly capacity of the plant is reported as 1500 metric tons of 3000 Mwd/ton Magnox fuel cooled for 130 days.[6]

Selection of Windscale as the site of the plant was said to be favored because the plant could be incorporated into the existing facilities, especially waste handling.[7] The philosophy of design and operation of the new plant is included in the description given in Sec. II.

It is reported that the U. K. Atomic Energy Authority (UKAEA) will modify its Windscale fuel-processing plant to enable it to handle oxide fuels by 1968. These changes are being made to accommodate the processing of oxide fuels from Britain's Advanced Gas-Cooled Reactor (AGR) and other European reactors.[8]

The UKAEA has signed a contract with Enta Nazionale per l'Energia Elettrica (ENEL) to recover plutonium from the Latina nuclear power station in Italy. This large-scale commercial processing contract, said to be worth several million pounds sterling, covers the full fuel load of 70 metric tons/year of the 200-Mw(e) reactor up to 1970. The economics is said to be favorable to reuse of plutonium as a substitute for ^{235}U in the Italian Società Elettronucleare Nazionale (SENN) and Società Elettronucleare Italiana (SELNI) power stations. Shipments are to start in mid-1965. Shipping, indemnities, and insurance will be handled by UKAEA.[9]

The UKAEA and the German fuel-fabricating firm Nuklear-Chemie und -Metallurgie G.m.b.H. (NUKEM) have set up a company to provide

fuel-manufacturing and -processing services "within the European community and especially in Germany." The new company, named Nukleardienst G.m.b.H., will have its headquarters at Wolfgang bei Hanau am Main, where NUKEM is located. The UKAEA and NUKEM hold equal shares in the new firm.[10]

Processing Plant in India

A fuel-processing plant has been completed at Trombay, India, to handle irradiated aluminum-clad natural-uranium fuel elements from the Canada India Reactor as well as future reactors. The plant employs chemical decladding, nitric acid batch dissolution, and solvent extraction with pulsed perforated-plate columns using 30% TBP (Purex type process). The solvent-extraction scheme employs a codecontamination cycle, a partition cycle, and two separate parallel cycles for the purification. The dissolver total volume is approximately 3500 liters, and the columns are 4 to 5 in. in diameter. Details of the plant, including waste-storage facilities, are given in Ref. 11, a 1964 Geneva Conference paper.

Provisional costs are reported as the following:[11]

Main process building complete with process equipment, utilities, general services, and plutonium facility	$5,300,000
Waste treatment and storage	2,000,000
Engineering costs	400,000
Total	$7,700,000

Developments at the Pilot Plant at Kjeller, Norway

Experience with the Norwegian-Dutch processing pilot plant at Kjeller, Norway, is described in a 1964 Geneva Conference paper, Ref. 12. This plant was put into operation in 1961, and the original purpose of producing research quantities of plutonium has been superseded by testing various flow sheets based on the Purex process. Some runs have been performed for the Eurochemic Company to evaluate decontamination factors.[12]

The Swedish AB Atomenergie has also installed an additional facility for processing studies that are currently devoted to the Silex (silica-gel) process.[12]

Thus far only fuel from the JEEP reactor at Kjeller has been processed.[12] Plant capacity,[13] based on an earlier description, was given as 3 metric tons/year for continuous operation, with a possible expansion to 10 tons/year.

Recent Processing Plans in the United States

Nuclear Fuel Services (NFS), Inc. (a subsidiary of W. R. Grace & Co.), has completed a new plant at Erwin, Tenn., to manufacture fuel-grade UO_2 of any enrichment. However, as with the existing plants, the operation does not include fuel-pellet production. The new plant, which replaces three smaller plants at Erwin, will be able to recycle uranium recovered at the NFS chemical processing plant at West Valley, N. Y.[14]

General Electric (GE) Company has begun to play a significant role in converting uranium hexafluoride to uranium dioxide and in manufacturing uranium dioxide fuel pellets. Not long ago GE began operating a pilot plant for UF_6-UO_2 conversion at its Vallecitos, Calif., facilities. A recent U. S. Atomic Energy Commission (AEC) shipment of UF_6 to the Vallecitos pilot plant was a 5313-lb consignment of 2.35% enriched uranium, which is ultimately destined for the Humboldt Bay reactor of Pacific Gas & Electric Co. This enrichment is lower than that previously specified for this reactor (2.6%), and the change indicates that the new fuel will be clad in zirconium rather than in stainless steel.[15]

Other firms currently receiving major amounts of UF_6 for conversion are Nuclear Fuel Services, Inc. (Erwin, Tenn.), Nuclear Materials & Equipment Corp. (Apollo, Pa.), United Nuclear Corp. (Hematite, Mo.), and Kerr-McGee Oil Industries, Inc. (Cushing, Okla.).[15]

The AEC proposes to issue a license to California Nuclear, Inc., Lafayette, Ind., for radioactive waste storage at Hanford. This will be the first license to a private firm for use of land leased by the AEC to the State of Washington. The company will sublease 100 acres of land from the state and will construct two buildings in connection with its operations of receiving, processing, and packaging of wastes that will be stored in the area.[16]

A hot pilot plant for development of fluidized-bed fluoride-volatility processing technology will be built and operated at the Oak Ridge National Laboratory (ORNL). This is part of

the AEC program to complete development of fluoride-volatility processing through "cold" engineering, "cold" semiworks, and "hot" pilot-plant programs by mid-1969. The principal objectives of the hot pilot plant will be to demonstrate (1) the separation of plutonium and uranium from fission products and (2) the recovery of plutonium by fluidized-bed fluoride-volatility methods. These separation and recovery steps will be demonstrated on an engineering scale. Problems of scaling up the pilot-plant equipment are being studied on a nonradioactive basis by personnel of the Engineering Development Department at the Oak Ridge Gaseous Diffusion Plant. Engineering Development Department personnel will also be actively participating in the design of the Fluidized-Bed Fluoride-Volatility Pilot Plant. Fuel elements clad in either stainless steel or Zircaloy-2, such as those used in the Commonwealth Edison Company's Dresden Nuclear Power Station, will be considered as the reference feed material for the pilot plant. Fluidized-bed methods for fuel processing have been studied in the United States at both Brookhaven and Argonne National laboratories, and Argonne will provide most of the process information required to design the plant.[17]

Design studies are just beginning. Installation of process equipment should occur during fiscal years 1966 and 1967, and operations should be concentrated in fiscal years 1968 and 1969. The major operations to be performed in the pilot plant are chemical decladding, fluorination, condensation of mixed hexafluorides, and product preparation.[17]

Economics of the Fuel Cycle

Projections of Fuel-Cycle Costs in the United Kingdom

Fuel-cycle costs for a large nuclear power program based on UKAEA cost projections for 1970 to 1980 have been discussed in Ref. 18, a two-part Geneva paper. Unit costs are summarized in Table I-1 for two methods of reporting costs: (1) fuel-inventory and replacement charges and (2) equivalent processing costs for the various steps of the fuel cycle. The Magnox reactors use natural-uranium fuel with magnesium-alloy cladding, and the AGR type reactors use slightly enriched UO_2 fuel with stainless-steel cladding. The reference processing plant is the new Windscale plant described earlier, which employs solvent-extraction separation. The cost projections for processing and reprocessing are said to have an uncertainty of ±20%. The cost figures assume ^{235}U fueling.

The reprocessing cost estimates in Table I-1 provide for processing the fuel to uranyl nitrate and plutonium nitrate and include a

Table I-1 ILLUSTRATIVE SHORT-TERM FUEL-CYCLE COSTS[18] PROJECTED FOR 1970 TO 1980

[5000 Mw(e) Assumed for Each Reactor Type. Costs Are in Mills per Electric Kilowatt-Hour]

	Standard Magnox	Early AGR		Standard Magnox	Early AGR
Inventory charge	0.43	0.47	Fabrication cost	0.73	0.77
Replacement charge:			Net uranium cost	0.80	1.13
Net uranium minus plutonium credit	0.16	0.72	Reprocessing cost	0.27	0.19
Processing	0.78	0.75	Plutonium credit	−0.43	−0.15
Total (rounded)	1.4	1.9	Total (rounded)	1.4	1.9

Notes:
1. Load factor, 85%; per annum interest, 7½%; amortization, 25 years.
2. Natural-uranium ore at $7 per pound.
3. Enriched uranium supplied and credited at a cost based on the present U. S. price scale offset at low enrichments by optimum blending with $7 ore.
4. Plutonium credited at $7 per gram for thermally fissile isotopes. (Total plutonium is $5.60 per gram for 3000 Mwd/ton Magnox fuel.)
5. Magnox equilibrium burnup is 4000 Mwd/ton (channel average).
6. AGR burnup is 12,000 Mwd/ton (channel average).
7. Processing and reprocessing costs are as in Table I-2.
8. Magnox thermal efficiency is 0.30; AGR is 0.40.
9. Original unit costs are in d/u.s.o. converted to mills per electric kilowatt-hour by multiplying by 11.65. This assumes 1 pound sterling equals 2.80 U. S. dollars.

capital sum sufficient to cover the perpetual storage of highly active, long-lived fission-product wastes. Fabrication thus starts with fuel in the nitrate form. Fabrication and reprocessing elements of the fuel-cycle costs also include items for transporting both new and irradiated fuel. Individual cost elements incorporated in Table I-1 for shipping, reprocessing, and fabricating are given explicitly in Table I-2.

Table I-2 REFERENCE COST ELEMENTS FOR FUEL-CYCLE UNIT COSTS*[18]

	Fuel type	
	Magnox†	AGR‡
Fabrication	16.5	64.5
Reprocessing	8.4	16.8
Transport of new fuel	0.14	0.64
Transport of irradiated fuel	0.70	2.8

*Costs are in dollars per kilogram of uranium. Monetary units are converted to dollars at a nominal rate of 1 pound sterling equals 2.80 U. S. dollars.
†Metal fuel.
‡Oxide fuel.

The above cost projections do not include research or development costs or liability insurance on plant or transport. (Apparently the costs reported also do not include overhead charges, which, in more detailed studies, are listed under contractor's overhead, engineering, insurance, working capital, etc.)

In Ref. 18 the potential minimum total fuel-cycle costs are estimated to be 1.0 mill/kw(e)-hr for the Magnox and AGR fuels. This future long-term minimum represents a greater proportional cost lowering for oxide than for metal fuel for the reference costs shown in Table I-1. The minimum costs for oxide fuel assume increased burnup to 20,000 Mwd/ton; it is estimated that little economic incentive would exist for further increase in burnup because of the compensating effect of decreasing throughput of the processing plants. General economic aspects of the fuel cycle are also discussed in Ref. 18.

Cost Study of Radiochemical Plants

A new cost study of production-scale aqueous processing of reactor fuels[19] has been presented by Du Pont as a supplement to an earlier publication[20] reviewed in this journal.[21] These studies were made under contract with the AEC with the aim of employing the experience of those associated with the Savannah River Plant to develop reference designs for future production-processing plants.

The basic reference-plant specifications in these studies were for an instantaneous throughput of 10 tons/day with a low-cost design using modern, proven process concepts. The earlier studies dealt with six cases:

Case I	A remote-maintenance plant for processing 10 tons of aluminum-clad natural uranium per day
Case II	A plant similar to case I but using contact maintenance
Case III	A remote-maintenance plant like case I but scaled down to 1 ton/day
Cases IV to VI	Plant additions and modifications of case I; capacity, 10 tons/day but with cladding of zirconium and stainless steel or either of these materials

A plant factor of 80% was adopted in cases I to VI (Ref. 19).

In the new study, case VII is presented for a plant capacity of 10 tons/day with a variant of maintenance philosophy, namely, that of "limited maintenance." Limited maintenance is defined in this study as providing for the replacement of equipment with moving parts or items "where susceptibility to failure from wear, pluggage, or other factors is significant. All other equipment items and piping are to be designed and built to specifications which would make them likely to last indefinitely in the intended service. No provisions are made in the design to facilitate their repair or replacement." The only other variation in case VII with respect to case I is the reduction of solution storage volume, which requires greater use of in-line instrumentation.[19]

Total plant costs for cases I, II, and VII are compared as follows:

	Case I, remote maintenance	Case II, contact maintenance	Case VII, limited maintenance
Total plant cost	$60,000,000	$70,000,000	$58,000,000
Annual operating cost	$6,234,000	$6,380,000	$6,380,000

The significance of the above costs is given as the following:

1. The lower plant cost for case VII compared to case I results mainly from the reduced size of the canyon building and the reduced canyon-piping costs. The lower piping costs re-

sulted from the elimination of remote-operated jumpers and their auxiliaries. The limited-maintenance plant is adapted to a fixed process that is not expected to change, and lower incidence of day-to-day maintenance is expected. On the other hand, the remote-maintenance plant can be more rapidly adapted to major process changes. The case I estimate included a 5% contingency, and the case VII estimate thus falls within the case I variance.

2. The lower plant cost of case VII compared to case II results from the elimination of duplicated equipment in case II, which allowed for continuity of production even through periods of major-equipment repair. Since the difference in costs for these two cases falls outside the contingency estimate of 5%, the difference is considered significant.

3. The operating cost for case VII is estimated to be the same as that for case II, which is slightly higher than that of case I. Variances of operating cost are estimated to be ± 20%, and therefore the differences in operating costs are not considered significant.[16]

It appears from this study that a limited-maintenance concept for a nominal capacity of 10 tons/day allows a reduction in process building and equipment costs by eliminating items that would provide reserve process flexibility and continuity of operation. These reductions, however, were within the estimated variances for previous reference cases for remote- and contact-maintenance plants.[19]

Transport of Irradiated Fuel

Development and evaluation of satisfactory methods of shipping irradiated fuel have continued to be a major subject of concern. A review of the latest practices and procedures for licensing in the United States was presented at the Symposium on Shipment of Radioactive Materials at the 57th Annual Meeting of the American Institute of Chemical Engineers.[22] Sequential accident test conditions (Part 71, Title 10 of the *Code of Federal Regulations*) are the following: (1) free fall from a height of 30 ft, striking an essentially unyielding surface in such a position as to suffer maximum damage; (2) a puncture drop test; (3) a specified fire; and (4) total immersion under 3 ft of water. Failure under these conditions is considered to occur if any of the following result: an effective multiplication factor (k_{eff}) in excess of 0.9, reduction of shielding to increase any external radiation level by a factor of 100, or release of more than 100 curies of activity from the cask. Experimental tests have already indicated cask designs capable of withstanding the mechanical damage conditions, and experiments are planned for the fire test, which stipulates exposure for 30 min with an 800°C source of radiant heat. Typical designs are cited in the report.[22]

A 1964 Geneva Conference paper (Ref. 23) gives transport costs based on French experience. The basic cask designs described are lead-shielded cylindrical shipping containers for irradiated fuel which have natural air convection (external) for cooling and a total rating of 8 kw for fission-product heat dissipation. Costs of such casks are reported to be about $2.50 and $1.80 per kilogram of cask weight for cask weights of 18 and 55 metric tons, respectively. For both cask sizes the shielding was about 21 cm of lead.[23]

A comparison was made between two methods of shipping 120-day-cooled spent fuel from the EDF-2 and EDF-3 power reactors at Chinon to the processing plant at the Hague, a distance of 350 km. In the first method (case A), all road shipment was used with a motor convoy of 35 metric tons, which is the maximum allowed in France without special formalities. For this method a cask of 22.5 metric tons was designed with a uranium capacity of 400 kg. In the second method (case B), a mixed road-rail container was used with a cask of 55 metric tons. In case B the short road sections, totaling 25 km, were such that permanent special authorization was readily obtainable. The round-trip costs for the two cases are compared in Table I-3, with case B showing the lower total unit cost. Although the total investment per kilogram of uranium shipped was nearly the same in both cases, transportation and insurance costs were substantially lower per kilogram of uranium in case B owing to the fewer trips and the less hazardous avenue of shipment.[23]

Other Geneva Conference papers (Refs. 24 and 25) also discuss the shipping of irradiated fuel in continental Europe.

Experience in the transport of irradiated fuel by the UKAEA is discussed in a 1964 Geneva Conference paper, Ref. 26. Some fea-

tures of the three major casks in use are given in Table I-4. Although no unsatisfactory experience has been encountered, the cast-iron casks do not have the impact strength of the high values considered by various agencies for newer specifications.[26]

The UKAEA is planning to extend its transport services in the area of transporting overseas fuel to UKAEA processing plants. In the last two years, irradiated fuel from the Danish DR-3 reactor and the Australian HIFAR (materials testing) reactor has been processed at Dounreay. In both cases the fuel was transported by sea and rail using materials-testing-reactor casks.[26]

A Magnox-fueled power reactor is in operation in Italy (Latina), and a similar reactor is being built in Japan (Tokai-Mura). Current assessment of such shipping conditions is under way. Although water-filled casks of the Central Electricity Generating Board (CEGB) type (Table I-4) appear to be less costly than air-cooled types, the use of water coolant must be carefully evaluated relative to loss of cooling and

Table I-3 COMPARATIVE COSTS IN FRANCE FOR SHIPPING SPENT POWER FUEL[23]

	Case A		Case B	
Reference conditions				
Cask weight, metric tons	22.5		55	
Cask fuel load, kg of U	400		2160	
Trips per year	600		100	
Number of casks	15		4	
	$	$/kg of U	$	$/kg of U
Round-trip costs*				
Rail transport			1147	0.53
Road transport	560	1.40	456	0.21
Amortization† (five years)	300	0.75	1708	0.79
Nuclear hazard insurance	690	1.72	1550	0.72
Total trip cost	1550	3.87	4861	2.25

*Dollar values are converted from francs at the nominal rate of five francs equals one U. S. dollar.

†Cask and special vehicles. Case B includes special facilities for rail-to-road transshipment.

Table I-4 UKAEA CASKS IN USE[26]

	Approximate cask weight, metric tons*	Capacity		Cost, $/kg of cask weight	Comment
		Kg of fuel	Kw		
Materials testing reactor	15	4.6†	2	1.3‡	1956 design, cast iron; cooling (internal and external) by natural air convection
Chapelcross	40	§		0.35‡	Early design, cast iron, 140 elements; internal cooling by natural water convection; external cooling by natural air convection
CEGB	50	2000¶	8.5	0.84‡	Fabricated steel cask; to be used for new shipments from power stations; same cooling as Chapelcross

*One metric ton equals 1000 kg.

†Elements of the materials-testing-reactor type contain 4.6 kg of ^{235}U.

‡Monetary units are converted to dollars at a nominal rate of 1 pound sterling equals 2.80 U. S. dollars.

§A total of 140 Magnox elements.

¶A total of 2000 kg of Magnox low-enrichment power-reactor fuel.

Table I-5 AEC-OWNED PATENTS (FOREIGN AND DOMESTIC) HAVING SPECIAL CONNECTION TO FUEL PROCESSING

Patent No.	Issuance date	Patent title
	U. S. Patents[27,28]	
3,135,599	June 2, 1964	Production of Uranium Metal Powder in a Fluidized Bed and Powder Resulting Therefrom
3,136,599	June 9, 1964	Plutonium Recovery from Nuclear Fuel
3,136,600	June 9, 1964	Separation of Actinides from Each Other
3,136,715	June 9, 1964	Process of Removing Ruthenium from Aqueous Solutions
3,140,151	July 7, 1964	Method of Reprocessing UO_2 Reactor Fuel
3,140,193	July 7, 1964	Process for Producing Oxidation Resistant Refractory Coating on Dense Graphite
3,141,911	July 21, 1964	Process for the Fabrication of Nuclear Fuel Elements
3,145,078	Aug. 18, 1964	Method of Reprocessing Nuclear Fuel Elements
3,146,064	Aug. 25, 1964	Decontamination of Uranium
3,147,109	Sept. 1, 1964	Separation of Plutonium, Uranium, Americium, and Fission Products from Each Other
3,148,941	Sept. 15, 1964	Dissolution of Uranium-Molybdenum Reactor Fuel Elements
3,150,924	Sept. 29, 1964	Pretreatment of Uranium Dioxide To Promote Its Conversion to Uranium Tetrafluoride
	Belgian Patents[29]	
632,265	May 13, 1963	Insolubilization of Fission Products
633,323	June 6, 1963	Separation of an Actinide Metal from an Alloy
634,616	July 8, 1963	Plutonium Recovery from Nuclear Fuel
634,617	July 8, 1963	Method of Dissolving Plutonium
635,023	July 16, 1963	Process for Preparation of Uranium Metal
637,669	Sept. 20, 1963	Preparation of Uranium Monosulfide
638,163	Oct. 3, 1963	Plutonium Oxide Spheres and Method of Making
638,375	Oct. 8, 1963	Plutonium Recovery from Neutron-Bombarded Uranium Fuel
639,069	Oct. 23, 1963	Paste Reactor
	Canadian Patents[30]	
661,150	Apr. 9, 1963	High Density Nuclear Fuel Composition
661,947	Apr. 23, 1963	Separation of Uranium and Plutonium Oxides
666,204	July 2, 1963	Processing of Uranium-Metal-Containing Fuel Elements
671,187	Sept. 24, 1963	Production of Uranium Monocarbide
	Canadian Patents[30] (Continued)	
672,052	Oct. 8, 1963	Preparation of UO_2 for Nuclear Reactor Fuel Pellets
672,422	Oct. 15, 1963	Actinide Carbide Product and Method of Making
672,423	Oct. 15, 1963	Dissolution of Uranium Fuels
672,811	Oct. 22, 1963	Preparation of High-Density Compactible Thorium Oxide Particles
672,939	Oct. 22, 1963	Separation of Europium from Other Lanthanide Rare Earths by Solvent Extraction
674,021	Nov. 12, 1963	Preparation of Refractory Oxide Microspheres
679,532	Feb. 4, 1964	Spray Calcination Reactor
681,035	Feb. 25, 1964	Dimensionally Stable, Corrosion Resistant Nuclear Fuel
682,789	Mar. 24, 1964	Fused Reactor Fuels
683,031	Mar. 24, 1964	A Process of Dissolving Fuel Elements of Nuclear Reactors
683,044	Mar. 24, 1964	Fuel Composition for Nuclear Reactors
684,926	Apr. 21, 1964	Method for Separating Transplutonium Elements from Rare Earth Fission Products
	French Patents[31]	
1,320,962	Feb. 20, 1962	Ceramic Coated Fuel Particles
1,323,871	Apr. 27, 1962	Preparation of Spherical Uranium Dioxide Particles
1,323,900	May 7, 1962	Method for Preparing UO_2 Compacts
1,326,725	May 14, 1962	Separation of Uranium Metal from Oxides and Slag in the Reduction of Uranium Tetrafluoride
1,332,378	Aug. 22, 1962	Dissolution of Uranium Fuels
1,335,555	July 3, 1962	Separation of Europium from Other Lanthanide Rare Earths by Solvent Extraction
1,339,020	Sept. 14, 1962	Fluorination of Oxidic Nuclear Fuel
1,339,745	Oct. 30, 1962	A Process of Dissolving Fuel Elements of Nuclear Reactors
	German Patents[32]	
1,112,791	May 13, 1960	Fused Reactor Fuels
1,117,029	Sept. 9, 1959	Method for Coating Graphite with Niobium Carbide
1,117,312	July 1, 1959	Method for Purifying Uranium
1,118,470	Aug. 21, 1959	Removal of Certain Fission Product Metals from Liquid Bismuth Compositions
1,118,770	July 25, 1959	Fused Salt Process for Recovery of Values from Used Nuclear Reactor Fuels

evolution of hydrogen from radiolysis and to corrosion of the Magnox fuel over long shipping times. Current tests show the desirability of providing refrigeration for rail and sea transport to maintain cask temperatures at about 10°C; at this temperature the hydrogen evolution is relatively low. Other alternatives are being considered also.[26]

Patents Available for Licensing by AEC

The Commission has announced a number of AEC-owned patents, domestic and foreign, on which it will grant licenses for royalties. Inquiries may be made to the AEC Office of Assistant General Counsel for Patents, Washington, D. C., 20545. From a total of 280 patents, those in Table I-5 are cited because of special connection to the fuel-cycle processes.

(W. J. Mecham and A. A. Jonke)

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Research and development carried out since 1958 on aqueous processes for the recovery of fissionable materials were covered in a general way in the proceedings of the Third United Nations International Conference on the Peaceful Uses of Atomic Energy, held in Geneva in 1964. A good review of the papers on fuel processing was recently provided by Vogel.[1] Much of the work reported at Geneva had been discussed earlier in *Reactor Fuel Processing*. This issue, however, covers work reported at Geneva which has not been previously discussed in this journal.

Preparation of Fuels for Recovery

Mechanical and chemical decladding procedures, as used in England, France, and Norway, are described, and methods for the dissolution of uranium carbide fuels are reviewed.

Mechanical Processing Methods

Two papers on processing, which included mechanical decanning as a first step, were presented at the Third Geneva Conference. Gaudernack, Lindland, and Joseph[2] describe a very simple underwater process used in a fuel-processing pilot plant at Kjeller, Norway, for decanning a fuel from the Joint Establishment Experimental Pile (JEEP) reactor. Each element consists of 13 pieces of uranium, 1 ft long by 1 in. in diameter, canned in two aluminum tubes with graphite end plugs. The use of a cutoff wheel to separate the end plugs caused dust to be produced when the fuel was penetrated. However, when the cutoff wheel was replaced with a hydraulic shear, water contamination was reported at only 10^{-4} $\mu c/cm^3$.

Corns et al.[3] describe a much more extensive decanning operation used at Windscale. An entire building 234 ft long, 50 ft wide, and 65 ft high is devoted to this operation. Decanning equipment is located in various cells. Master-slaves with 100-lb lifting capacity and $ZnBr_2$ windows are installed at intervals. Two powered manipulators and a $1\frac{1}{2}$-ton hoist are available at the machines, and the building is serviced by a 35-ton crane for each handling. Fuel from the Magnox program has been decanned successfully.

Magnesium-Cladding Removal with Sulfuric Acid

The French gas-cooled power reactors make use of uranium fuel that is clad in magnesium. The bulk of the magnesium is removed mechanically, but in the normal process it is necessary to treat the declad rods with cold dilute HNO_3 to remove small amounts of magnesium which still adhere. Faugeras and Chesne have recently reported[4] that the mechanical decladding step, along with the dilute HNO_3 treatment, could be eliminated by decladding with cold (<50°C) 1*N* H_2SO_4. The magnesium dissolves rapidly (~0.5 mm/hr), and the attack on the uranium is negligible. A disadvantage would be the presence of sulfate in the waste.

Dissolution of Irradiated Carbide Fuels

The carbides of uranium and plutonium are potentially attractive fuels for high-temperature power reactors. Extensive work[5] at Oak Ridge National Laboratory (ORNL) has been reported earlier on the preparation of these materials for solvent extraction recovery by hydrolysis with water or HNO_3. Since low-temperature hydrolysis is markedly inhibited by irradiation and since in the absence of pyrohydrolysis HNO_3

oxidizes part of the carbon to soluble organic compounds that might be expected to interfere with solvent extraction, processing alternatives have been sought. Flanary et al.[6] have recently described a method for pyrohydrolysis of carbides which appears capable of overcoming the difficulties just noted.

Conversion of irradiated UC to a material suitable for nitric acid dissolution is effected with reasonable speed by treatment with steam at 750°C. As the temperature is lowered, the reaction becomes very much slower and is not complete in 7 hr at 650°C. The gaseous products of the reaction are hydrogen, carbon dioxide, and a small amount of CO. In the absence of air (a necessary condition to avoid the formation of explosive off-gas mixtures), the solid product is UO_2 containing a small amount of carbon. A small fraction of the cesium present is volatilized during oxidation.

Five tests were performed using this pyrohydrolysis procedure with 4- to 7-g pieces of UC that had been irradiated to between 7500 and 16,000 Mwd/metric ton. After treatment with steam at 700 to 800°C for up to 5 hr, the product dissolved in 30 min in 6.5*M* nitric acid. The uranium and plutonium present were then readily and completely recovered by tributyl phosphate (TBP) extraction. In another series of seven hot-cell tests on material irradiated to 7500 Mwd/metric ton, the pyrohydrolysis was conducted for 2 to 3 hr at 700 to 750°C. Typical dry off-gas compositions were 80 to 83% hydrogen, 11 to 16% CO_2, and 4 to 6% CO. A sample of 20% PuC–80% UC, irradiated to 20,000 Mwd/metric ton, was also pyrohydrolyzed successfully at 750°C for 2 hr. Uranium and plutonium were recovered satisfactorily from all products by TBP extraction after HNO_3 dissolution. The gamma decontamination factor effected in one cycle was about 10^4. A suggested flow sheet for stainless-steel-clad UC fuel, based on pyrohydrolysis, is shown in Fig. II-1.

For comparison, similar irradiated UC samples were dissolved directly in 60% HNO_3. Almost half of the carbide carbon remained in solution, primarily as organic acids. The organic impurities were largely, but not completely, eliminated by oxidative degradation (i.e., by refluxing with 11*M* HNO_3, or with 0.2*M* $KMnO_4$). Extraction by TBP of the treated uranium solution proceeded satisfactorily except that 0.4% of the plutonium was not recoverable. It was conceived that such organic impurities would be likely to build up in an extraction system and cause further difficulties or that their presence in waste streams would be deleterious.

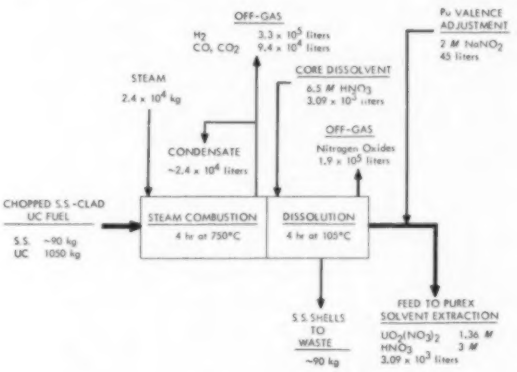


Fig. II-1 Pyrohydrolysis process for uranium carbide reactor fuel.[6]

Efforts were also made to effect the direct water hydrolysis of irradiated carbide fuels at 80 to 100°C but with little success. For example, UC irradiated to 6500 Mwd/metric ton was only about 60% hydrolyzed after two weeks in water at 80°C. In another test a sample of 80% UC–20% PuC irradiated to 800 Mwd/metric ton was exposed to water at 80°C for 26 hr. Only 0.005% of the plutonium was leached from the sample.

Solvent-Extraction Processes

One of the recent Geneva Conference papers was a Russian report[7] of successful hot pilot-plant studies of a TBP process in which carbon tetrachloride was used as a diluent. Methods of removing TBP and its degradation products from process streams are reported by U. S. investigators.[8] Both American[9] and Russian[10,11] authors have described the chemistry of heavy-element separations and its application to processes. Characteristics of some of the newer extraction reagents for uranium, plutonium, and thorium are also described.[12,13] Later in this section the flow sheets for the Eurochemic fuel-processing installation at Mol,

Belgium,[14] are discussed under the heading Plant and Equipment Design and Operation.

TBP Extraction Processes

Pushlenkov et al.[7] have described the results of testing a Purex type flow sheet, proposed for power-reactor fuel processing, which incorporated a noninflammable diluent, provision for neptunium recovery along with recovery of uranium and plutonium, and the extensive use of back-cycle techniques to minimize waste volumes and product losses. The scale of operations was 8 to 12 kg of uranium per day, and the beta-activity level of the feed ranged from 50 to 200 curies/liter. The nature of the fuel processed and specific details of feed preparation were not given, other than a UNH concentration of 1.1*M* and an acidity of 2*N* HNO_3. An extractant concentration of 1.1*M* TBP in CCl_4 was used throughout, and extractions were conducted in mixer-settler units, of which there were six sets of varying numbers of stages (two sets contained three units each, and four sets contained two units each).

The process flow sheet[7] shown in Fig. II-2 is basically similar to one resulting from work in the United States in which CCl_4 diluent was used.[15,16] Compositions of some principal streams are given in Table II-1. Partition of uranium from plutonium is effected in the first cycle (I Cycle) by $Fe(NO_3)_2$ stabilized with N_2H_4, and both the uranium and plutonium streams are subjected to two additional decontamination cycles. The neptunium is separated from the uranium in the course of uranium decontamination and is collected in the raffinates (2U7 and 3U7) from II Uranium Cycle and III Uranium Cycle. The second and third plutonium-cycle raffinates (2Pu6 and 3Pu6) are combined with those from the uranium cycles and are concentrated greatly to yield an acidity

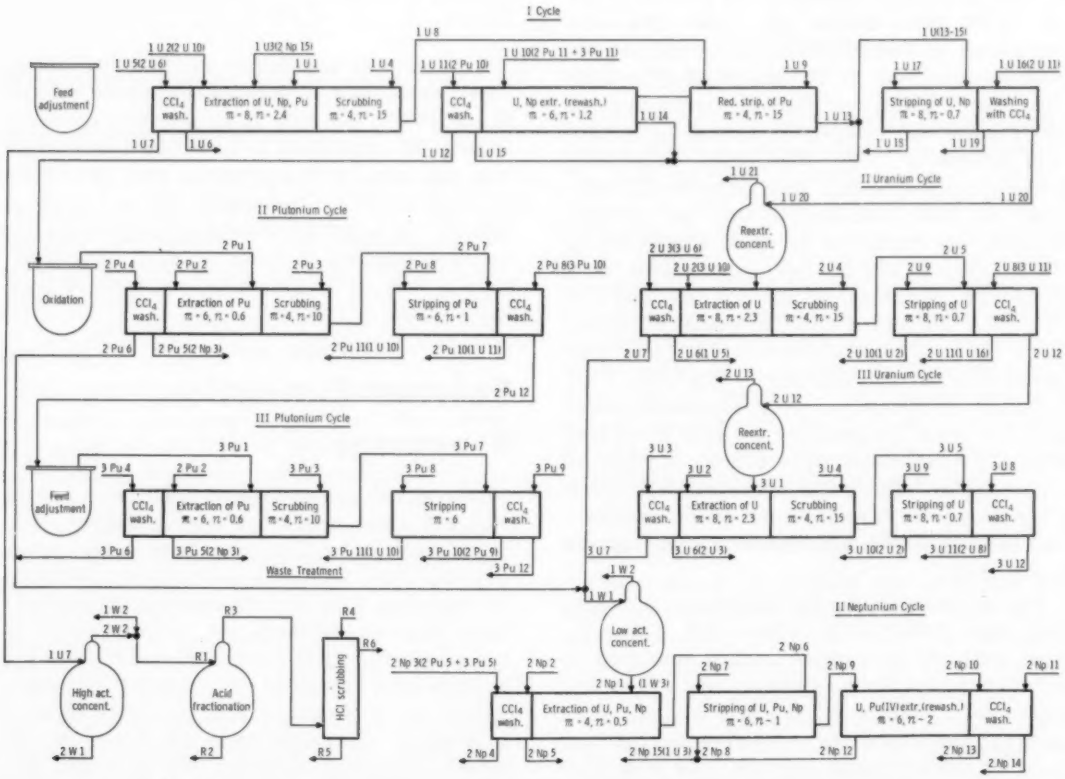


Fig. II-2 Purex type TBP-CCl_4 extraction process for recovery of uranium, plutonium, and neptunium.[7] The compositions of the principal feed streams are given in Table II-1. Here m is the number of stages and n (phase-flow ratio) is V_{org}/V_{aq}.

Table II-1 COMPOSITIONS OF SOME PRINCIPAL STREAMS FOR TBP-CCl_4 EXTRACTION PROCESS[7]

Streams	Composition
1U1	1.1*M* UNH, 2*M* HNO_3
1U2, 2Np2, 2Pu2	1.1*M* TBP in CCl_4
3U3, 2Np11, 3Pu9	CCl_4
2U4	1*M* HNO_3
3Pu3	2*M* HNO_3
1U4, 2Pu3	3*M* HNO_3
2Np7	0.1*M* $NaNO_2$
1U9	0.1*M* HNO_3, 0.1*M* $Fe(NO_3)_2$, 0.05*M* N_2H_4
1U17	Water (*p*H 2-3)
2U9, 3U9, 2Pu8	Water
3Pu8	Water, 0.05*M* N_2H_4

of 5*N* HNO_3 and to enable extraction of residual uranium and plutonium along with neptunium by TBP-CCl_4. Neptunium is transferred into a 0.1*M* $NaNO_2$ solution to yield the product of this cycle, and the recovered uranium and plutonium after extraction are rewashed into solvent and are returned to the original partition cycle. In this manner the only aqueous waste streams are a high-activity waste stream (1U7) from I Cycle and a low-activity waste (2Np4) from neptunium recovery, representing the combined uranium and plutonium second and third cycles. Aqueous product streams from all cycles are washed with CCl_4, fresh material being used for the final products. Fresh TBP-CCl_4 is fed to III Uranium Cycle and passes successively back to I Cycle; fresh solvent is also used in both plutonium cycles and is returned to the plutonium-partitioning mixer-settler. After use in the I Cycle, the extractant mixed with CCl_4 wash is regenerated by carbonate washing and by distillation of both components. The separation of CCl_4 and TBP is effected by azeotropic steam fractionation, and TBP is distilled at a pressure of 5 mm Hg.

The condensates produced by intercycle and final concentration of uranium streams are sufficiently pure to be used for stripping. Nitric acid is also recovered by fractionation. During this step a side stream is removed which contains 85 to 90% of the chloride formed in I Cycle by radiation-induced decomposition of extractant.

The uranium recovered is decontaminated from fission products by a factor of at least 2×10^6 and is separated from plutonium by a factor of 10^4. The plutonium stream, after oxalate precipitation, is decontaminated by a factor of 10^8 from fission products and by better than 10^5 from uranium. The neptunium is of similar quality. Because of the high initial acidity, zirconium-niobium decontamination in the I Cycle is effected only by a factor of ~250, but the alternation of oxidizing and reducing conditions in subsequent cycles, as well as varying acidity, permits adequate overall decontamination.

Solvent deterioration and corrosion did not appear to be major problems in the operation of this process over a one-year period. Radiolysis of the TBP (*G* value of 5 to 7 molecules/100 ev) led to the formation of 0.0001*M* dibutyl phosphoric acid in the solvent. This did not accumulate in the system. The yield of chloride was equal to 25 to 50 atoms/100 ev absorbed by CCl_4. A maximum of 0.004*M* HCl was found in the I Cycle raffinate. This concentration of HCl did not cause noticeable corrosion of the evaporation and extraction equipment, made of 18-8 chrome-nickel steel, and the corrosion rate of coupons in the equipment, including welded joints, did not exceed 0.1 mm/year.

A report[8] by Hahn et al. at the Idaho Chemical Processing Plant (ICPP) summarizes information previously discussed[17–19] on the behavior of TBP and its degradation products during enriched-uranium processing at the ICPP. Dibutyl phosphate (DBP) was found to be the principal deleterious product and was present in all first-cycle plant streams beyond the first extraction column. A mixer-settler with a hydrocarbon extractant removed TBP, but not DBP, from aqueous streams in accordance with laboratory distribution data. Hydrous ZrO was found to sorb DBP effectively, to be regenerable with NaOH, and to dissolve in 8*M* to 12*M* HNO_3 as a means of disposal.

Recovery of Transplutonic Isotopes

In the program of ORNL for the recovery and separation of major quantities of transuranic elements, it has been planned to effect the separation of the actinides from lanthanide fission products by extraction with a tertiary amine from concentrated LiCl solution.[20] Weaver and Kappelmann[9] propose a new process to effect this separation based on the stronger complexing of the trivalent actinides than of the lanthanides by an aminopolyacetic acid. This permits extraction of the latter elements and yttrium by a monoacidic organophosphate or

phosphonate. A number of complexing, extracting, and buffering reagents have been investigated, but in the tentative process illustrated in Fig. II-3, the sodium salt of diethylenetriaminepentaacetic acid (Na_5DTPA) is used as the complex former, lactic acid acts as the buffer, and the lanthanide extraction is effected with 0.5*M* di-2-ethylhexyl phosphoric acid (D2EHPA) in diisopropylbenzene. The actinides may be

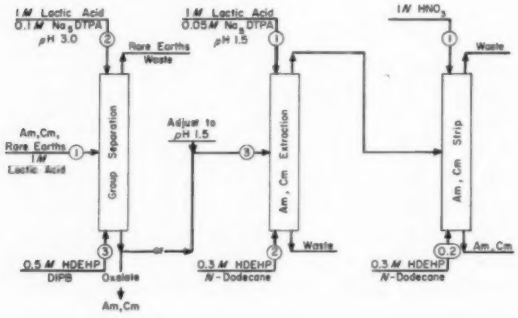


Fig. II-3 Flow sheet for purification of americium and curium.[9]

purified by oxalate precipitation or removed from the raffinate of the first extraction and purified by extraction with the same solvent in a different diluent (*n*-dodecane), from which they are stripped into dilute HNO_3. In this process single-stage separation factors between neodymium, the least extractable lanthanide, and americium are about 50. The application of this process to mixtures containing the transcurium elements has yet to be investigated, but it is believed to be feasible with some modifications.

In companion papers presented at the Geneva Conference,[10,11] the development of techniques employed by Russian workers for the isolation, purification, and separation of transplutonium elements was described. It is assumed that the starting material consists principally of fission products, plutonium, americium, and curium dispersed in magnesium and is dissolved in HNO_3. It was found that Pu(IV) could be extracted and efficiently separated from the actinides-lanthanides either by 0.2*M* thenoyltrifluoroacetone (TTA) in benzene, or by extraction with TBP, D2EHPA, trioctylamine, or tridecylamine (TDA) in inert diluents. The latter method is preferred for solutions containing large amounts of $Mg(NO_3)_2$. The effects of *p*H and the nature of the diluent on the TTA extraction procedure were found to be important. The use of an acetate buffer (*p*H 3.5) and of an oxygenated diluent such as amyl acetate resulted in the most favorable extraction. The actinide-lanthanide separation was best effected from concentrated LiCl solution by extraction with either D2EHPA or TDA, or preferably by the use of both reagents in turn. Again the nature of the diluent was important; with TDA dissolved in xylene, the separation factor for curium and europium was highest. For final purification of americium and curium, chromatographic elution from the cation-exchange resin KU-2 by ammonium α-oxyisobutyrate solution was employed.

New Types of Extractants

In continuing studies, reported earlier,[21] at the Ames Laboratory on the solvent-extraction characteristics of some bidentate organophosphorus compounds, Mrochek and Banks[12] have described work on a series of *bis*(di-*n*-hexylphosphinyl) alkanes in which the alkane chain was one to four carbon atoms in length. All were powerful complexing agents for uranium. From nitrate systems, distribution ratios varied from 250 to 1200 for 1*M* HNO_3 to 65 to 180 for 7*M* HNO_3, using a 0.05*M* solution of the complexing agent in dichlorobenzene. From $HClO_4$ solutions much wider ranges in distribution ratios were observed, both as a function of acidity and of ligand structure.

Alkylamines have increasingly been studied as extractants for nuclear fuels and transplutonic elements, particularly in the development of processes for the recovery of uranium and plutonium. Awwal[13] of the Pakistan Atomic Energy Commission reported at the Geneva Conference on the feasibility of amine extraction of thorium from sulfate systems in application to the Th-^{233}U cycle. Primary amines yielded only very low distribution coefficients, but distribution values obtained with secondary and tertiary amines such as di-*n*-octylamine, tri-*n*-octylamine, and methyl-didecylamine were adequate for consideration of rather dilute sulfate solutions.

Protactinium Separation

The isolation of short-lived ^{233}Pa (27-day half-life), produced from ^{232}Th, has been of

interest for cross-section measurements because of the importance of the nuclear properties of this isotope to the success of the Th-^{233}U fuel cycle, but its unavailability in quantity, intense radioactivity, and the limited knowledge of its chemistry have made it necessary to work with very small quantities until recently. At the Materials Testing Reactor, several hundred grams of thorium were irradiated at high fluxes to minimize loss by decay of the product. Codding et al.[22] recently described the separation of a gram of ^{233}Pa from this material. The process steps were basically simple, but processing operations were rendered complicated by the extremely high radiation level of the material (20,000 curies of ^{233}Pa), and the consequent rapid radiolysis of water and decay-heat emission. The thorium, containing about 1% protactinium, 0.4% uranium, and 0.05% fission products, plus metallic aluminum disks used as heat sinks, was dissolved in 13M HNO_3–0.1M HF. The protactinium was carrier precipitated three times with MnO_2 by the addition of $KMnO_4$ and was redissolved between the precipitations in H_2SO_4. Manganese was removed by leaching the final precipitate with HNO_3-H_2O_2, and the residual protactinium oxide was digested in H_2SO_4. The protactinium was finally precipitated as the iodate, which was thermally decomposed (by its own decay heat) to Pa_2O_5 for use in the cross-section measurements. Chemical analysis, gamma counting, and neutron-absorption measurements showed the absence of thorium, manganese, initial uranium, or other impurities in the final product. (C. E. Stevenson)

Plant and Equipment Design and Operation

An interesting design variation on pulse columns is described in a Russian paper.[23] The variation consists of making the holes through a thicker-than-average plate on a slant, thus imparting a rotary motion to the fluids. Data are presented for extraction of uranyl nitrate from an acidified water solution by diluted tributylphosphate (20%). The following conclusions were stated by the authors:

1. The average efficiency of sections of a pulse column with rotating flow does not depend on the feed rates to the column or on the relative phase volumes.

2. The dependence of the efficiency on the intensity of pulsing is expressed by a simple power equation.

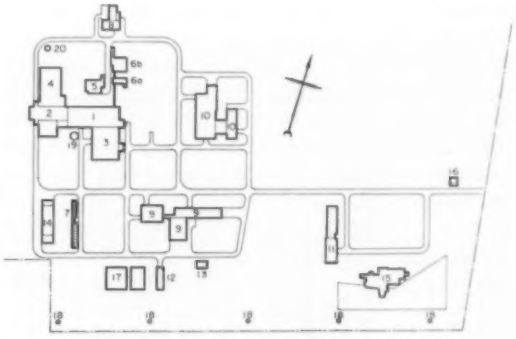
3. Simultaneously increasing the frequency of pulsation and decreasing the height of the sections increases the intensity of mass transfer in the column.

Also, observation of the data presented indicated that the efficiency for this system and conditions was not appreciably better than conventional design, although it would be predicted to be. (D. M. Paige)

Eurochemic Fuel-Processing Installation at Mol, Belgium

In Sec. I of this issue, a journal article[14] about the Eurochemic installation at Mol, Belgium, is reviewed briefly. Here additional details on plant layout, equipment, and flow sheets are presented. The overall site layout of the Eurochemic plant is shown in Fig. II-4.

A versatile "head-end" processing stage is required to cope with fuel elements of different sizes (up to 4 m in length) and having cores of varying composition. Cladding materials may be aluminum, magnesium (as "Magnox"), stainless steel, zirconium, or Zircaloy-2. Fuels may be uranium oxide or alloys with molybdenum or aluminum.



1, process building
2, fuel reception and storage building
3, analytical laboratory
4, ventilation building
5, high-level-waste building
6, final-product storage
7, inactive-liquids storage
8, effluent plant
9, general-services building
10, research laboratory
11, administration building
12, water-treatment plant
13, E.B.E.S. station (electricity)
14, inactive-solids storage building
15, canteen
16, guard building
17, sedimentation sump
18, wells
19, reservoir (200 m^3)
20, gaseous effluent stack

Fig. II-4 Site layout[14] of the Eurochemic installation. (Courtesy of EuroNuclear.*)*

Initially only one dissolver will be installed. It will be used both for decanning and for dissolution of fuel of up to 1.6% ^{235}U enrichment. The dissolver will be cylindrical, about 7 m long and 30 cm in diameter, and connected to a 3-m^3 recirculation vessel. The volume of reagent in the system will be sufficient to dissolve up to 1 ton of elements. The system will employ critically safe geometry.

The separations flow sheet uses two Purex solvent-extraction cycles. Flow schematics of the cycles are given in Figs. II-5 and II-6. In both cycles the vertical extraction columns utilize perforated plates and are pulsed by a compressed-air system. It is expected that gamma decontamination factors of 4000 and 50 will be achieved in the first and second cycles, respectively.

Following solvent extraction, a final purification step for the uranium product will utilize a silica-gel column that will remove the residual zirconium-niobium activity. It is expected to achieve a decontamination factor of about 15. A flow sheet is shown in Fig. II-7.

New British Fuel-Processing Plant at Windscale

A new British nuclear fuel-processing plant at Windscale, described in general terms in Sec. I of this issue, will have a capacity for 130-day-cooled Magnox fuel of 1500 metric tons/year and 3000 Mwd/ton.[24] Both uranium and plutonium will be recovered. The development and design of the plant and the plant-control methods have been discussed in two Geneva Conference papers.[3,24]

For the plant at Windscale, three design philosophies with regard to maintenance have been employed: remote maintenance, direct maintenance, and no maintenance. High-level engineering standards are employed in all three philosophies to minimize incidence of maintenance. Where no maintenance is employed, provisions for plant decontamination and entry by direct access have been made. Examples of application of these maintenance philosophies to various parts of the plant are as follows:

Remote maintenance	Mechanical decanning
Direct maintenance	Pumps, filters, sampling equipment, instruments
No maintenance	Fuel dissolution, active evaporation, most of solvent extraction

Components under direct maintenance are located in small shielded compartments exterior to the main biological shielding.[3]

Automatic equipment and centralized control have been used intensively in the new plant. Substantial reductions of personnel have been made accordingly. A data logger is installed in the central control room for integrated

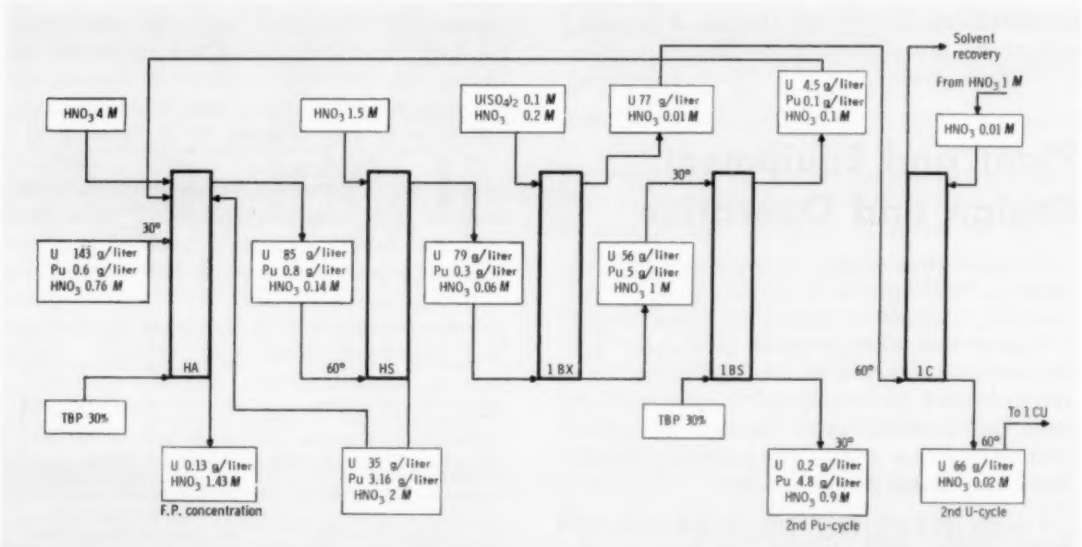

Solvent recovery
From HNO3 1 M
HNO3 0.01 M
HNO3 4 M
HNO3 1.5 M
U(SO4)2 0.1 M HNO3 0.2 M
U 77 g/liter HNO3 0.01 M
U 4.5 g/liter Pu 0.1 g/liter HNO3 0.1 M
30°
U 143 g/liter Pu 0.6 g/liter HNO3 0.76 M
U 85 g/liter Pu 0.8 g/liter HNO3 0.14 M
U 79 g/liter Pu 0.3 g/liter HNO3 0.06 M
U 56 g/liter Pu 5 g/liter HNO3 1 M
HA
60°
HS
1 BX
1 BS
1 C
TBP 30%
TBP 30%
To 1 CU
U 0.13 g/liter HNO3 1.43 M
F.P. concentration
U 35 g/liter Pu 3.16 g/liter HNO3 2 M
U 0.2 g/liter Pu 4.8 g/liter HNO3 0.9 M
2nd Pu-cycle
U 66 g/liter HNO3 0.02 M
2nd U-cycle

Fig. II-5 Flow sheet of the first extraction cycle.[14] *(Courtesy of* EuroNuclear*)*

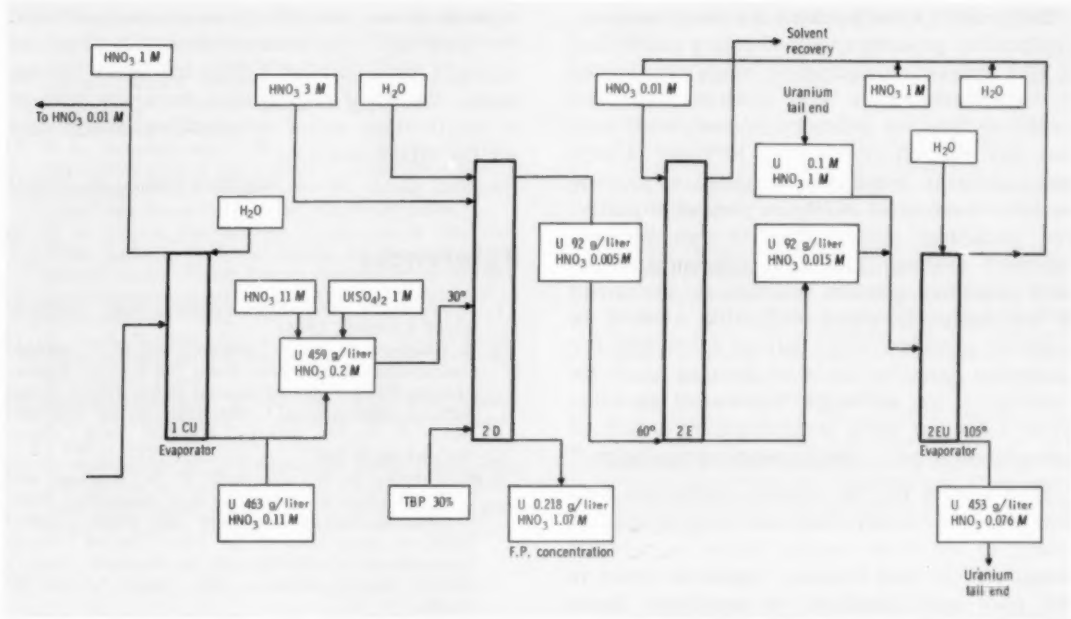


Fig. II-6 Flow sheet of the second extraction cycle.[14] *(Courtesy of* EuroNuclear*)*

receiving, control, and printing. The logger uses alternating current (rather than direct current) because of advantages in noise rejection and amplification. The frequency used is well separated from that of the standard power supply and its harmonics. Pressure, level, and density transmitters use simple elements incorporating differential transformers; temperatures are measured by platinum resistance thermometers.[3]

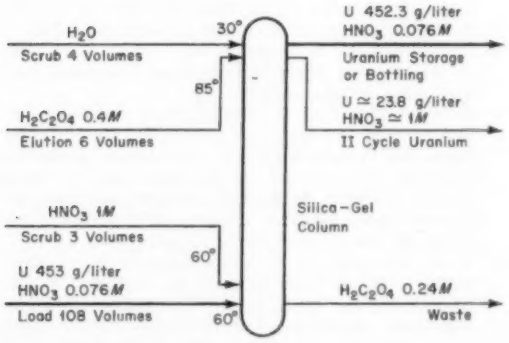


Fig. II-7 Flow sheet for uranium final purification.[14] *Silica-gel column data: volume, 44 liters; diameter, 0.2 m; height, 1.4 m. (Courtesy of* EuroNuclear*)*

Mechanical decanning was adopted to avoid radioactive wastes associated with chemical decanning. A continuous dissolving scheme previously used was retained with some improvements. An all-TBP solvent-extraction process was adopted rather than the previous Butex-TBP process because of more favorable operating costs and higher ruthenium decontamination, which reduced problems of effluent disposal. A three-cycle solvent-extraction scheme was used to meet specifications, with allowance for solvent degradation, operational variations, and future demands.[24]

Separation of uranium and plutonium in the second cycle (rather than in the first) was chosen for the following advantages:

1. The major activity in the second cycle was free of salts and could be evaporated without penalty for disposal to highly active waste storage.
2. One less cycle of purification was required in the plutonium stream.

These advantages were judged sufficient to outweigh the main disadvantage of "late separation," namely, two additional, nongeometrically safe contactors for unseparated uranium and plutonium.[24]

The product specifications for the plutonium-purification process required only a single line of TBP extraction equipment since two cycles of codecontamination with uranium had been employed. Nuclear safety by concentration control was adopted in this step. However, a second plutonium cycle was installed to provide an extra margin of safety on plutonium purity. The plutonium system has its own solvent-recovery system. The final concentration of pure-plutonium-product solution is performed in equipment in which criticality control is achieved geometrically. Solvent extraction for plutonium purification was favored over its alternative, ion exchange, because of the relatively advanced state of development of solvent extraction for safe, continuous plant operation.[24]

Flow sheets for the solvent-extraction system were developed from miniature pilot-plant trials, in which the scaling factor was several thousands. In this scheme residence times in the pilot unit identical to residence times planned for the plant unit were considered necessary to allow direct scale-up. In the pilot-plant runs, up to 90 mg of finely divided solids per liter was present in the dissolver product. These solids were separated in the bottoms and at the interfaces of the primary contactor; carry-over of "crud," often a problem with column units, was not encountered in the mixer-settler units.[24]

Analysis of nuclear safety by concentration control was analyzed by computer calculations. Checks were made experimentally of possible abnormal conditions.[24]

The mechanical decanner, as adopted, employed a hydraulically loaded three-wheel cutter. Less force was required to push the fuel rod through this cutter than had been required in the previously used punch-and-die decanner. The lower force is considered favorable for handling more brittle, higher-burnup fuel rods. The Magnox elements varied in length from 20 to 44 in., with rod diameters of 0.9 to 1.25 in. Decanning rates of at least one element every 2 min are required to match the plant processing rate. Prototype tests of the machine have been carried out.[24]

The choice of mixer-settlers instead of pulsed-column extractors was said to be made on the following points favorable to mixer-settlers: (1) slight advantage in capital cost, (2) greater process flexibility, (3) less carry-over of cruds, and (4) lower development cost for scale-up.[24] The features favorable to pulsed columns were smaller holdup and fewer moving parts. Chemical engineering work was done on a single-stage model to establish design data for the mixer-settlers.[24]

(W. J. Mecham and A. A. Jonke)

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Volatility Processes for High-Enriched Fuels

The methods employed in the processing of reactor fuels containing highly enriched uranium differ from those used for low-enriched fuels in two major respects: (1) since the concentration of uranium in the fuel is low (< 20%), the initial step of the processing scheme involves the separation of uranium from the fuel matrix, and the uranium is thereby freed for subsequent recovery by volatility methods; and (2) recovery of plutonium is not required for highly enriched fuels.

In the processing of alloy fuels containing enriched uranium, initial separation of uranium from the alloy is achieved by converting the alloying metal to a volatile chloride. Final recovery of uranium is achieved by fluorination to produce volatile uranium hexafluoride. Volatility processes are also being applied to graphite-matrix fuels containing enriched uranium carbide. Fluidization techniques have been applied to several volatility processing schemes for conducting the direct chemical conversion of fuel materials into gaseous compounds.

URANIUM-ALLOY FUELS

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium-zirconium alloy has been developed in France.[1,2] The process employs two principal steps in which chemical separation of the fuel constituents is accomplished by selective volatilization of chlorides and fluorides. In the initial step the zirconium alloy reacts with anhydrous hydrogen chloride at approximately 400°C to produce volatile zirconium tetrachloride and nonvolatile uranium trichloride. This reaction is carried out while the fuel element is immersed in a fluid bed of alumina particles. Uranium is recovered as UF_6 in the second step by the reaction of fluorine with UCl_3 at 200 to 300°C. The UF_6 product is purified by sorption-desorption in a series of sodium fluoride beds.

An industrial-scale facility was constructed at Brignoud, France, to evaluate the process as a means for recovering uranium from uranium-zirconium scrap material containing 6% uranium. A schematic diagram of the facility, which was designed to process 5 to 10 kg of alloy in a single batch, is shown in Fig. III-1. The fluid-bed reactor is constructed of nickel and is 3 mm in wall thickness, 20 cm in diameter, and 160 cm high. The reactor is charged with 50 kg of 70-mesh alumina (80-cm static-bed height) which serves as the fluid-bed material and in which the fuel material is immersed.

The gas leaving the fluid-bed reactor during the chlorination step is filtered by a packed bed of alumina particles before entering the $ZrCl_4$ condenser. Several filter concepts were evaluated, and, in the final design, the gas is filtered by downward flow through a bed of alumina particles contained in a vessel mounted within the disengaging chamber of the fluid-bed reactor (Fig. III-1). The filter vessel is 200 mm in diameter and 200 mm high. The packed-bed filter consists of two separate layers of alumina particles: 12.5 kg of 200-μ particles supported by 6.4 kg of 1200-μ particles. The entire bed is supported on a metal grill.

The hydrochlorination reaction is carried out using 4 m^3 of 100% HCl per hour at bed temperatures ranging from 350 to 500°C. Zirconium tetrachloride is collected in a condenser that is cooled with air or water. The rate of reaction between HCl and zirconium is automatically controlled by applying forced-air

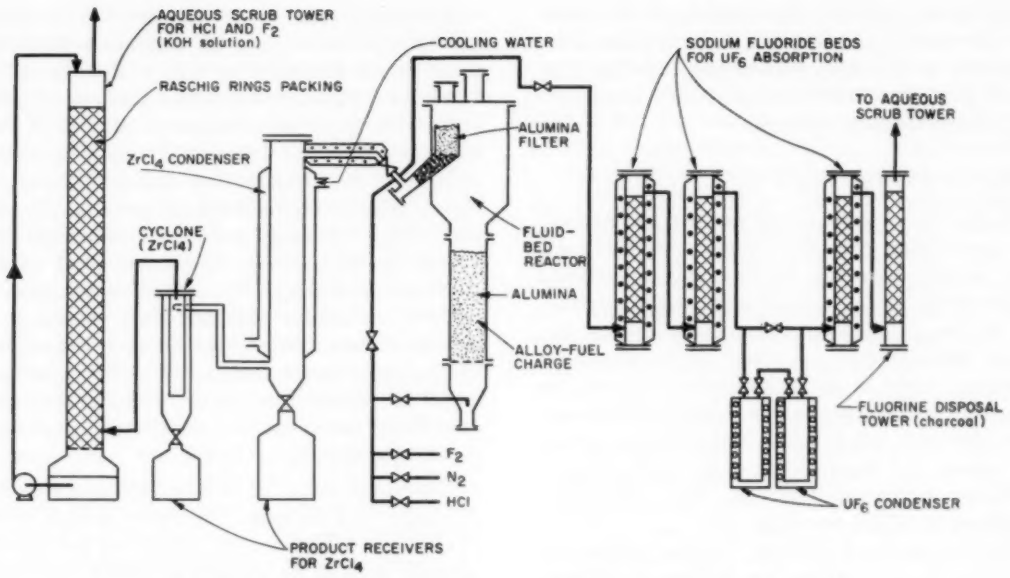

Fig. III-1 Flow sheet for processing uranium-zirconium-alloy fuel.[1]

cooling to the fluid-bed reactor when the bed temperature exceeds 450°C. At temperatures above 500°C, nitrogen is substituted for HCl to quench the reaction. The course of the hydrochlorination reaction is continuously monitored by measurement of the hydrogen concentration in the off-gas stream from the reactor. Average reaction rates of 1.7 kg of alloy per hour have been frequently achieved in demonstration runs using single charges of alloy. In instances where the hydrochlorination step is immediately followed by fluorination, the practice is to continue the HCl flow for at least 30 min after the hydrogen monitor has indicated that the reaction is complete to ensure that there is no unconverted metal remaining on the reactor. The system then is purged with nitrogen for 3 to 4 hr prior to introduction of fluorine. The HCl reaction rate, the HCl utilization efficiency, and the uranium inventory in the system are increased by successively hydrochlorinating up to 15 fuel charges prior to fluorination. Incorporation of this processing scheme has made it possible to attain hydrochlorination rates up to 3 kg/hr and HCl utilization efficiencies of 30 to 50%. About 25% of the uranium is collected on the packed-bed filter during hydrochlorination. Losses of uranium through the filter to the $ZrCl_4$ condenser are uniformly less than 0.2% of the total uranium fed to the reactor.

Recovery of uranium as UF_6 is achieved by passing fluorine, diluted with nitrogen, through the fluid bed and packed-bed filter at a total gas-flow rate of 500 liters/hr. Since this flow rate is less than that required to fluidize the alumina-bed material, a separate nitrogen-gas stream sufficient to produce fluidization is periodically introduced into the reactor to avoid continued channeling of the gas through the static bed during fluorination. The temperature of the alumina beds in the reactor and filter is maintained between 200 and 300°C. The fluorine concentration in the gas is progressively increased from 10 vol.% in nitrogen to nearly 100% during the course of the 2- to 4-hr fluorination period. Although the fluorine efficiency may reach 50% at the start of the reaction, the average efficiency is between 10 and 20%. The quantity of uranium remaining in the alumina bed including the filter-bed material is generally from 25 to 30 g, corresponding to a concentration of 500 to 600 ppm. Since this figure does not increase after a series of several reaction cycles, the alumina-bed material may be reused for additional cycles. The UF_6 product is purified by selective absorption on sodium fluoride at 100°C, followed by desorption at 400°C, and then is collected in refrigerated condensers maintained at −60°C.

Although the facility at Brignoud was primarily constructed to recover uranium from

scrap alloy, this unit has been used as a basis for the design of a hot pilot plant, under construction at Fontenay-aux-Roses, for the processing of irradiated uranium-alloy fuels by a fluid-bed volatility process.[2]

Graphite-Matrix Fuels

Engineering-scale investigations on methods for processing graphite–uranium carbide fuels are being conducted at Brookhaven National Laboratory (BNL).[3] These studies are applicable to the High-Temperature Gas-Cooled Reactor (HTGR) fuel or other fuels containing uranium carbide in a graphite matrix. The proposed processing scheme consists basically in oxidation of the graphite and uranium carbide by oxygen and fluorination of the oxide residue (ash) by elemental fluorine, with subsequent purification of the resulting UF_6.

Two methods of burning the fuel have been considered: (1) burning the fuel in a fluidized bed of inert particles such as alumina particles and (2) burning in a fixed bed of fuel. The first method is being extensively investigated at BNL; the fixed-bed burning concept is being developed at Oak Ridge National Laboratory (ORNL) and has been described in previous issues of *Reactor Fuel Processing*.[4–6]

A facility has been constructed at BNL[3] for demonstrating the fluid-bed oxidation-fluorination process as shown in Fig. III-2. The Nickel 201 alloy fluid-bed oxidizer consists of a 4-in.-diameter reaction section 8.3 ft long topped by an 8-in.-diameter disengaging section 3 ft long. A water-cooled chamber above the disengaging section serves as an off-gas cooler and filter housing for the stainless-steel porous-metal filters. The outer wall of the reaction sections is finned and surrounded by an 8-in.-diameter Inconel shell forming an annulus through which cooling air is circulated. The alumina-bed material (−40 +140-mesh alumina) is transferred pneumatically, after fuel oxidation, from the bed receiver to the fluorinator through ½-in. tubing.

The fluorinator is a 4-in.-diameter Nickel 201 pipe 12.3 ft long. The lower portion of the reactor is cooled by air circulated through the annulus formed by an Inconel sheath surrounding the reactor. Attached to the top flange of the fluorinator are two Monel porous metal filters that are provided with a pulsed-gas blowback system.

High-boiling fluorides in the UF_6-containing gas stream from the fluorinator are collected in a condenser maintained at 25°C. The UF_6

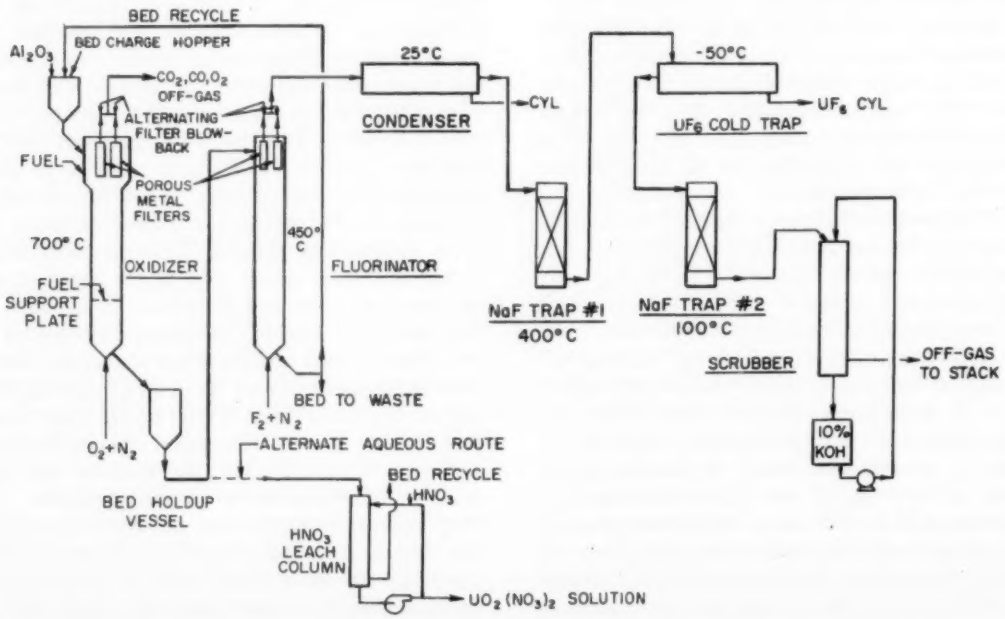

Fig. III-2 Continuous-oxidation–batch-fluorination pilot-plant flow sheet for graphite fuels.[3]

stream is further purified by passing through a NaF trap at 400°C. The uranium hexafluoride product is collected in a condenser at −50°C.

A series of oxidation-fluorination demonstration tests has been made in the facility with prototype uranium carbide–graphite fuel. For the oxidation step approximately 4 kg of fuel was charged to the oxidizer, the alumina bed was fluidized with nitrogen, and the unit was heated to 625 to 650°C. At this point the nitrogen was replaced by 100% oxygen as the fluidizing gas at 1.4 cfm. The oxidation reaction was regulated by forced-air cooling of the reactor to hold the wall temperature to a maximum of 710°C. In continuous operation fuel was added as needed to keep the oxygen utilization (or burning rate) high. Bed material was continuously withdrawn to the product receiver from the bottom of the oxidizer.

Although the reaction rate (kilograms of carbon per hour) increased as the oxygen feed rate increased, the oxygen utilization decreased as the feed rate increased. In this facility an oxygen feed rate of 1.4 cfm appeared to be optimum. At this flow rate the average burning rate was 1.24 kg of carbon per hour, and the oxygen utilization was 96%. An average heat-transfer coefficient from the fluid bed to the reactor wall of 85 Btu/(hr)(sq ft)(°F) was calculated. An average temperature difference of 30°C was calculated for the bed centerline and outside wall temperatures.

Fluorination of the ash in the product from the fluid-bed oxidizer was carried out as a batch operation. The initial period of the fluorination reaction was conducted at 450°C with a feed gas containing 25 vol.% fluorine in nitrogen. During the course of the reaction, the fluorine concentration was slowly increased to 50 vol.%. Uranium recovery by fluorination in five tests averaged 99.2%, based on the residual uranium in the alumina-bed material and in the fluorinator after fluorination.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

Several processes that involve separation methods based on the volatility of uranium halides are being developed for the processing of uranium dioxide fuel elements. Laboratory-scale studies on the development of low-decontamination processes for UO_2 based on the volatility of uranium chlorides are being carried out at several research centers.[7–12]

The U. S. Atomic Energy Commission's (AEC) Division of Reactor Development has established as a goal the completion of development of fluoride-volatility processing technology for low-enrichment fuels including hot-pilot-plant operation by July 1, 1969. Therefore a fluidized-bed fluoride-volatility pilot plant for irradiated fuels is planned for installation and operation at Oak Ridge National Laboratory (ORNL).[13] This facility will be used to demonstrate the separation of plutonium and uranium from fission products in low-enrichment power-reactor fuels and will be used in the recovery of plutonium. The major operations to be performed in the pilot plant are: (1) decladding, (2) fluorinating, (3) condensing the mixed volatile fluorides, and (4) preparing the uranium and plutonium products. The processing flow sheet that is to be demonstrated in the pilot plant is based on process-development work currently under way at Argonne National Laboratory (ANL). Further details of the fluoride-volatility pilot plant are presented in Sec. I of this issue.

CHLORINATION OF URANIUM DIOXIDE

Gens[7] at ORNL is investigating on a laboratory scale a method for processing UO_2 fuels based on reaction of the oxide fuel with carbon tetrachloride and chlorine to form volatile chlorides of uranium and plutonium. In the absence of chlorine, nonvolatile $PuCl_3$ rather than volatile $PuCl_4$ is formed by reaction of CCl_4 with PuO_2. Equations were developed for calculating the capacity of chlorine for transporting $PuCl_4$ as a vapor from the reaction zone. It was determined that the presence of UCl_5 and UCl_6 has little effect on the capacity of chlorine to oxidize $PuCl_3$ to $PuCl_4$. On the basis of thermodynamic calculations, a practical set of operating conditions for volatilization of uranium and plutonium from UO_2 fuels containing up to 1 wt.% PuO_2 would be reaction at 550°C with a gas containing 85 vol.% chlorine and 15 vol.% CCl_4.

A method for separating uranium from certain other elements that may be present in UO_2 fuels based on volatilization of chlorides and selective condensation of UCl_4 has been described by Ishihara and Hirano.[12] A series of tests was performed with irradiated UO_2 to determine the decontamination effected by chlorination of the fuel with CCl_4 at 400, 500, and 600°C. A simple chlorination–fractional distil-

lation process was not successful in completely separating fission products from uranium; cerium was the main fission product that condensed with the uranium chloride. Admixing of natural CeO_2 with the UO_2 fuel prior to chlorination markedly decreased the level of cerium activity in the uranium chloride condensate. Uranium recovery during chlorination was significantly improved by absorbing UCl_4 on a bed of sodium chloride as compared with the collection of UCl_4 by means of condensers. This step was successful in purifying the uranium from zirconium, niobium, and molybdenum.

A method for processing ceramic fuels of low enrichment based on the fractional sublimation of chlorides is being developed at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium.[8–11] Prior to chlorination the uranium dioxide fuels are oxidized to U_3O_8 and then reduced to UO_2 to obtain a fine powder that is highly reactive toward the chlorinating reagents. Uranium dioxide may be completely converted to volatile UCl_6 by reaction with a gaseous mixture of CCl_4 and chlorine. Several techniques have been studied to improve decontamination in the process cycle

$$UO_2 \text{ (or } U_3O_8) \xrightarrow[Cl_2]{CCl_4} UCl_6 \xrightarrow[H_2]{H_2O} UO_2$$

Two schemes that involved the formation of fission-product chloride double salts were investigated to improve uranium decontamination during the chlorination step.[11] When this process cycle is used, certain fission products, such as zirconium and niobium, form volatile chlorides that are not easily separated from volatile uranium chlorides. These fission-product chlorides, however, do form double salts with certain inorganic chlorides that exhibit negligible vapor pressures even at high temperatures. In one scheme the irradiated U_3O_8 is mixed with a suitable inorganic chloride salt, and the mixture is chlorinated with a gaseous mixture of CCl_4 and chlorine so as to produce volatile UCl_6 and concurrently fix the fission products in double chloride salts. Chlorination of U_3O_8 at 300°C in the presence of NaCl or KCl hinders the volatilization of UCl_6. In the presence of $ZnCl_2$, LiCl, or CsCl, the chlorination reaction is retarded or incomplete. Other salts such as $MgCl_2$, $CdCl_2$, $NiCl_2$, $CoCl_2$, $BaCl_2$, and $CaCl_2$ neither affect the volatilization of UCl_6 nor exert any selective retention of fission products. In the other scheme the chlorination of irradiated U_3O_8 produces a mixture of UCl_6 and volatile chlorides of the fission products. This mixture is passed through a layer of inorganic chloride salts in such a manner as to fix the fission products as double salts but without fixing the uranium. Although some fission products can be separated from uranium in this manner, zirconium and niobium chlorides cannot be separated since these chlorides have a lesser tendency to form nonvolatile complexes than has UCl_6.

A modified chlorination procedure based on the formation of a nonvolatile stable complex between phosphorus oxychloride and uranium tetrachloride has been studied as a means for separating uranium from zirconium and niobium.[8–11] The process involves the reaction between UO_2 and PCl_5 to form the complex UCl_4-$POCl_3$. The corresponding $POCl_3$ complexes with zirconium and niobium chlorides are volatile at 600°C, whereas the uranium complex is considerably less volatile. Although a significant decontamination in niobium and zirconium is achieved using this procedure, the decontamination is only selective for niobium and zirconium, and, because of the high stability of the uranium complex, further separation of uranium from other fission products is difficult. Therefore the procedure involving the use of PCl_5 as a chlorinating agent has been abandoned.

FLUORIDE-VOLATILITY PROCESSES

Workers at CEN[8–11] are developing a fluorination process for the recovery of uranium from UO_2 fuel (also containing PuO_2) based on the initial conversion of the oxide to UF_4 prior to fluorination to UF_6 in order to minimize fluorine requirements. All reactions in the process,

$$UO_2 \text{ (PuO}_2) \xrightarrow{O_2} U_3O_8 \text{ (PuO}_2) \xrightarrow{HF} UO_2F_2 - UF_4 \text{ (PuF}_4) \xrightarrow{F_2} UF_6 \text{ (PuF}_6)$$

have been studied in fluid-bed equipment.

In the initial processing step, the sintered oxide fuel is activated for hydrofluorination by an oxidation procedure in which finely divided U_3O_8 is produced. The oxidation reaction is carried out in a fluid-bed reactor at 450 to 530°C using a gas stream containing 20 vol.% oxygen in nitrogen. A quantity of granulated

alumina equal in weight to the UO_2 is used as the inert bed material. The oxidation rate was observed[11] to decrease as the degree of organization of the UO_2 crystal lattice increased. The presence of fission products in the UO_2 also reduced markedly the rate of oxidation. And in tests performed with UO_2 containing 3 to 40 wt.% PuO_2, the oxidation rate was always less than that obtained with pure UO_2. Complete oxidation of fuel with high plutonium content was not obtained at temperatures below 475°C. On the basis of these observations, it is expected that the oxidation rate of highly irradiated UO_2 fuel containing plutonium will be significantly less than the oxidation rate of pure unirradiated UO_2.

Initial development work on the processing cycle included a step in which U_3O_8 was reduced by NH_3 to UO_2 prior to reaction with HF to form UF_4. The formation of agglomerates during the reaction between HF and finely divided UO_2, and the considerable processing time required for the reduction and hydrofluorination steps, prompted discard of this reaction sequence in favor of the direct hydrofluorination of U_3O_8, which does not lead to extensive agglomerate formation. Hydrofluorination of U_3O_8 is carried out at 450°C using 50 vol.% HF in nitrogen. A series of tests has been performed to evaluate the reactivity of U_3O_8-PuO_2 mixtures toward HF to produce a fluoride mixture containing PuF_4, UF_4, and UO_2F_2. It was observed that the rate of reaction of mixed oxide containing 3 to 10 wt.% PuO_2 with HF is nearly identical to that obtained with pure, unsintered UO_2. The rate of reaction of U_3O_8-PuO_2 mixtures containing 40% PuO_2 is very low.

Fluorination of the mixed fluorides to UF_6 and PuF_6 is carried out at 450°C with 2 to 15 vol.% fluorine in nitrogen. Control of the reaction is achieved by regulating the fluorine concentration in the fluidizing gas. The final portion of the uranium is recovered by fluorination with 25 vol.% fluorine at 525°C. Results of tests involving the processing of 4 kg of U_3O_8 in fluid-bed equipment indicated that the average conversion to UF_6 was greater than 99.5% and that fluorine utilization was approximately 60%.

Operations for Separation of Uranium and Plutonium

Of major concern in the development of the fluoride-volatility process for low-enriched UO_2 fuel is establishing methods for the separation of uranium from plutonium and for the recovery of plutonium. One method under development at CEN[8-11] involves the absorption of the UF_6-PuF_6 mixture in a bath of molten salts such as NaCl-KCl or LiCl-KCl. Under the influence of oxygen-containing substances, the fluorides are transformed into a soluble uranyl oxyhalide and insoluble PuO_2. After separation of the PuO_2, uranium is recovered as UO_2 by electrolytic reduction. Further details on this technique for separating uranium and plutonium in fused-salt media are given near the end of Sec. III (see page 104).

An alternative method for effecting the separation of uranium from plutonium involves the selective fluorination of uranium from the mixed fluorides (UF_4-UO_2F_2-PuF_4) with chlorine trifluoride.[9-11] Plutonium is recovered as PuF_6 in a subsequent step by fluorination of the residual PuF_4 with fluorine. In tests performed in a fluid-bed reactor, the reaction between UF_4-UO_2F_2 and ClF_3 proceeded rapidly at 100 to 150°C with 99.9% conversion to UF_6. The reaction rate of UF_4 with ClF_3 is higher than that of UO_2F_2. There has been no indication[10] that any reaction occurs between PuF_4 and ClF_3.

An alternative approach for processing power-reactor fuels, being studied at CEN,[8-11] involves the oxidation of the fuel or an intermediate compound to uranium trioxide prior to fluorination with sulfur tetrafluoride to form uranium hexafluoride. Sulfur tetrafluoride is a selective fluorinating agent for converting U(VI) compounds to UF_6, whereas plutonium compounds are converted to PuF_4. The process cycle involves the following reactions:

$$UO_2\ (PuO_2) \xrightarrow{HNO_3} UO_3\ (PuO_2)$$

$$\xrightarrow{SF_4} UF_6\ (PuF_4) \xrightarrow{F_2} (PuF_6)$$

Oxidation of UO_2 to ϵ-UO_3 is carried out at 350°C with a gaseous mixture of nitric acid vapor and oxygen. The reaction temperature must be carefully regulated to avoid the formation of the γ-UO_3 polymorph that is considerably less reactive to SF_4 than ϵ-UO_3.

Recent studies[10] have shown that the conversion of PuF_4 to PuO_2 and of UF_4 to UO_3 can be readily accomplished with a mixture of nitric acid vapor and oxygen at 350°C. The conversion rate for PuF_4 to PuO_2 is signifi-

cantly faster than the rate for the conversion of UF_4 to UO_3.

The reaction between SF_4 and UO_3 to produce UF_6 and SOF_2 is carried out at 300°C. Although laboratory-scale static-bed tests have demonstrated complete conversion of UO_3 to UF_6, tests performed in fluid-bed equipment have indicated incomplete conversion because of deposition of UF_4 adjacent to the reaction zone. Investigations on the separation of uranium and plutonium by this technique have shown[11] that the reaction proceeds slowly and that the separation is incomplete owing to the formation of UF_4. The difficulties associated with the application of the SF_4 fluorination method to the processing scheme have caused this technique for effecting a separation of uranium from plutonium during the fluorination step to be abandoned in favor of the ClF_3 method.

Pilot-Scale Facility for Processing Ceramic Fuels

A pilot-scale alpha-gamma facility is being constructed at CEN[14] to study the remote chemical processing of spent ceramic fuel materials by fluidization techniques. The primary objective in the operation of the facility is to observe the behavior of uranium, plutonium, and fission products during the volatilization operations in a fluidized bed on a 4- to 5-kg scale. The program includes experiments on sintered UO_2 that have been subjected to various degrees of irradiation, on UO_2-PuO_2 mixtures, on UC fuel, and on UC-PuC mixtures. Initial efforts, however, are directed toward processing of lightly irradiated sintered UO_2 according to the following process scheme:

1. Oxidation:

$$3UO_2 \text{ (sintered)} + O_2 \rightarrow U_3O_8 \text{ (powder)}$$

2. Hydrofluorination:

$$U_3O_8 \text{ (powder)} + 8HF \rightarrow [UF_4 + 2UO_2F_2] \text{ (powder)} + 4H_2O$$

3. Fluorination:

$$[UF_4 + 2UO_2F_2] \text{ (powder)} + 5F_2 \rightarrow 3UF_6 \text{ (gas)}$$

These chemical reactions take place in a fluidized bed of alumina particles at a temperature of approximately 450°C. The process equipment includes a mechanical decanner, a fluid-bed reactor that includes a disengaging chamber and a bank of sintered-metal filters, a cyclone separator for collection of solid fission products, and a UF_6 collection and recovery system.

The facility consists of two separate alpha boxes. All chemical reactions and separations are carried out by remote manipulation in the larger box, which is shielded with a 15-cm-thick lead wall. The UF_6 recovery system is contained in the adjacent box, which is shielded with a 5-cm-thick lead wall. (J. J. Barghusen)

Fluoride-Volatility Processing of Fuel from Molten-Fluoride Thermal-Breeder Reactors

The status of the general technology of molten-salt thermal-breeder reactors has been reviewed in published papers that were initially presented at an information meeting on the Molten-Salt Reactor Experiment (MSRE) at ORNL.[15] This development program is one of those concerned with the long-range utilization of nuclear resources, particularly via the Th-^{233}U fuel cycle. Seventeen papers covering the physics, chemistry, engineering, and materials are given, including outlines of the status of corrosion and chemical processing studies. Summarized are the potential advantages of fluid-fuel reactors in general and molten-fluoride reactors in particular. Both fluorides and chlorides are considered promising for reactor applications on the basis of conveniences in the following: fuel preparation, fuel management in the reactor, and chemical processing. Fluorides are said to be preferred for thermal reactors, but for fast reactors the neutron-energy moderating properties of fluorides are a serious disadvantage. For fast reactors chloride mixtures using ^{35}Cl would be expected to be preferred.[15]

In the processing of fuel from molten-fluoride reactors, the fluoride-volatility processes for separating uranium as UF_6 from the other components of the discharged fuel can be readily utilized. The molten-salt fluoride-volatility process, especially the recent pilot-plant work at ORNL, has always been considered for this application. The molten-salt fluoride-volatility process has been reviewed extensively in *Reactor Fuel Processing*, and in Ref. 16 a description of the ORNL pilot-plant work was given. A specific process for molten-fluoride reactor fuel has been reviewed and a

tentative flow sheet presented in Ref. 17. In this process ^{233}U is first separated as UF_6 by fluorination of the molten salt; then aqueous methods are used to recover the salt for reconstitution of fuel. The solvent salt stream is separated from the thorium-fission-product stream, which may then be further treated for recovery of thorium.

A design study and cost estimate for a volatility-processing scheme applied to a 1000-Mw(e) molten-fluoride reactor of the single-zone converter type was reviewed in a previous issue (Ref. 18). This study did not include aqueous steps to recover salt or thorium.

Conceptual Fuel-Processing Steps for ORNL Molten-Salt Breeder Reactor

In the present MSRE progress report (Ref. 15), the conceptual fuel-processing steps are those shown in Fig. III-3. The core fuel cycle is shown at the right of the reactor and the blanket fuel cycle at the left of the reactor. Uranium-233 is recovered from the blanket as the decay product of ^{233}Pa.

Krypton and xenon are removed in the reactor by sparging the fuel salt with helium in the pump bowl. The off-gas is passed through charcoal beds, where the fission products are absorbed and the helium is recycled to the reactor.

Side streams of fuel and blanket salt are removed from the reactor for processing in a facility at the reactor site. The complete fuel and blanket charges, respectively, are processed in 10 to 60 days (3 to 15% burnup of fissile material) and in 35 to 200 days (equivalent to 300 to 1700 Mwd per metric ton of exposure). The fuel salt is first treated with fluorine to convert the UF_4 to UF_6 that is swept out of the fluorinator. The UF_6 is then reduced back to UF_4 with hydrogen in a flame reducer and returned to the reactor.

The uranium-free salt, containing fission products, is dissolved in 90% hydrofluoric acid. Rare earths and zirconium salts are insoluble in this acid and are separated from it by filtration. The solution, containing lithium and beryllium fluorides and some soluble fission products (principally Cs, Rb, Sr, Ba, Re, Se, Nb, Cd, Ag, and Te), is next evaporated to dryness. Part of the salt is discarded to rid the system of a portion of the soluble fission products; the rest of the salt is melted, combined with the recovered uranium, and returned to the reactor.

The blanket salt is fluorinated to remove the bred uranium as the hexafluoride, sparged with helium to remove traces of fluorine, and recycled directly to the blanket. Since only a small fraction of the blanket material fissions, the fission-product-removal step is unnecessary. The fission-product poison level is controlled by replacing the blanket salt on a 20-year cycle. Protactinium is not removed from

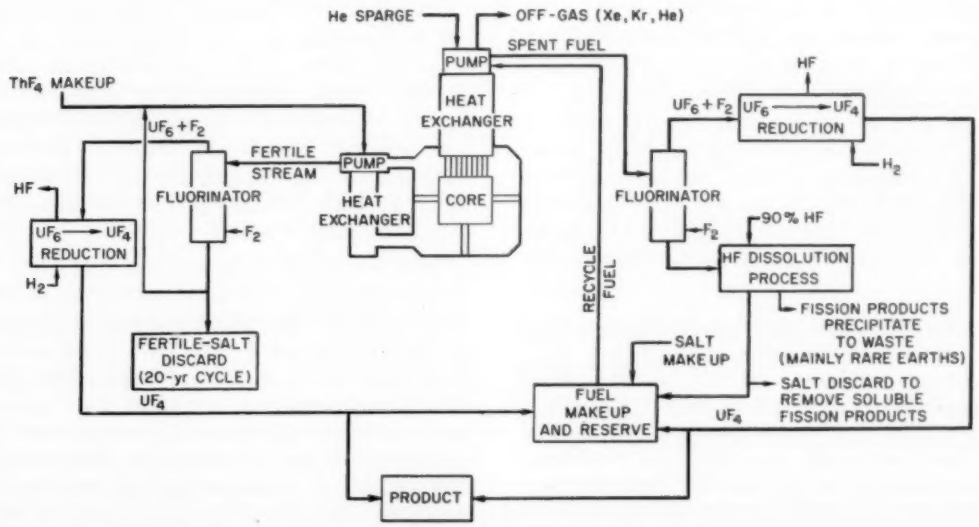

Fig. III-3 Conceptual fuel-processing steps for the ORNL molten-salt breeder reactor.[15]

the fertile stream in this process; its concentration rises until the decay rate equals its production rate. Loss of neutrons to protactinium is controlled by adjusting the volume of the fertile salt.

The UF_6 from the fertile-stream fluorinator is reduced to UF_4 with hydrogen and blended with the fuel stream for recycle to the reactor. Excess product is sold.

Single-Region Graphite-Moderated Reactor, Fuel-Processing Facility, and Salt-Preparation Facility

The present program of the MSRE is intended to develop the technology of circulating-fuel molten-fluoride thermal reactors with associated fuel-cycle processes through operation of a 10-Mw(t) single-region graphite-moderated unit. In the present MSRE concept, a basic ^7LiF-BeF_2 salt is used for core fuel, blanket fuel,* and coolant. A salt secondary coolant (rather than NaK, for example) was chosen for safety reasons. The core fuel contains fissile uranium as UF_4 and also about 5 mole % ZrF_4 to prevent formation of relatively insoluble UO_2 in case of oxygen contamination. The compositions and properties of these reference salts are given in Table III-1. A discussion of the phase diagrams and other chemical aspects of these salt systems is given in Ref. 15.

Table III-1 COMPOSITION AND PROPERTIES OF FUEL AND COOLANT SALTS[15]

	Fuel	Coolant
Composition, mole %		
LiF	65	66
BeF_2	29.1	34
ZrF_4	5	
UF_4	0.9	
Liquidus temperature, °F	842	851
Physical properties	At 1200°F	At 1062°F
Density, lb/cu ft	146	120.5
Heat capacity, Btu/(lb)(°F)	0.455	0.526
Viscosity, centipoises	7.6	8.3
Thermal conductivity, Btu/(hr)(sq ft)(°F/ft)	3.2	3.5
Vapor pressure	Negligible	Negligible

The fuel-processing facility for the MSRE has two functions. The first is to remove any oxide accumulation in the molten salt by sparging the salt with a mixture of hydrogen and hydrogen fluoride. The second is to recover uranium from the molten salt by sparging with fluorine and volatilizing the uranium as uranium hexafluoride. This second function should not be required until a program using the 30% enriched fuel ends. At that time all uranium-bearing salts will be fluorinated to remove the uranium of this enrichment. For the next phase of the program, 93% enriched uranium will be added to the fuel salt.

The facility will handle 75-cu ft batches of salt, which is about the volume of blanket salt that would be processed daily in a 1000-Mw(e) thermal-breeder station on an 80-day cycle. The cost of the facility will be about $350,000.

A schematic drawing of the MSRE fuel-processing system is shown in Fig. III-4. The fuel-processing facility is separated from the drain tanks by freeze valves (FV). The spent salt from the reactor system is introduced into the fuel-storage tank, where processing takes place. If the salt is fully irradiated fuel salt, a decay time of four days is required before transfer to allow for xenon decay, since the fuel-processing facility is not vented through the large charcoal beds. If transfer of a fully irradiated fuel batch is desirable before 26 days' decay, it will be necessary to cool the batch in the fuel-storage tank. This can be done by circulating the cell-ventilation air through a space around the tank.

Additional information on the economics of the molten-fluoride processing system is provided by costs of the salt-production facility of the MSRE program. The salt-production facility is reported to have a probable replacement cost of $300,000 to $500,000. Operation, maintenance, and equipment costs are budgeted at an average $20,000 per month on a seven-day three-shift schedule.

Data on the fluoride starting materials that have been acquired for the production of MSRE materials are shown in Table III-2. The cost of the raw materials for the coolant and flush salt mixture, ^7LiF-BeF_2 (66-34 mole %), is $10.13 per pound. As calculated from operating and raw-materials costs, the coolant and flush salt mixture has an estimated value of $19.71 per pound. A similar cost for the fuel salt mixture, excluding ^{235}U, is estimated at $17.33 per pound. Thus the initial charge of coolant, flush, and fuel salt mixtures for the MSRE will

*The blanket fuel would contain thorium (as ThF_4) at concentrations of about 15 mole %. However, in the present development program, a blanket loop is not included.

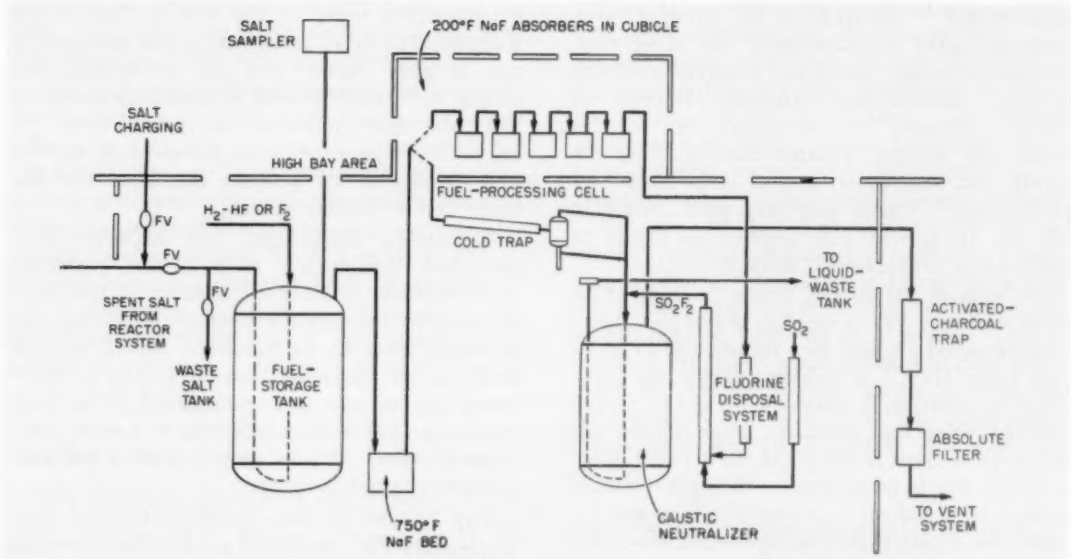

Fig. III-4 Molten-Salt Reactor Experiment fuel-processing system.[15]

Table III-2 COSTS OF RAW MATERIALS USED IN MSRE FLUORIDE PRODUCTION[15]

Material	Quantity in initial charge	Unit cost, $	Total cost, $
^7LiF	22,000 lb	16.50*	363,000
BeF_2	12,000 lb	5.70	68,400
ZrF_4	2,300 lb	8.00	18,400
UF_4	90 kg (^{235}U basis)	12,000.00	1,080,000
		Total	1,529,800

*Includes $1.82 per pound for preparation as fluoride salt.

have an estimated value of $496,400, exclusive of plant amortization and uranium costs.

A general review of the various chemical separations considered for molten-fluoride reactors, including experimental work done at ORNL and Harwell, has been published by Dawson and Sowden.[19] (W. J. Mecham)

Pyrometallurgical Processes

A review article, by Lawroski and Burris, on the processing of reactor fuel materials by pyrometallurgical methods has been published in the *Atomic Energy Review*,[20] the journal of the International Atomic Energy Agency. The article traces the development of pyrometallurgical processes for spent nuclear fuels from their inception to the present and discusses the principles of many pyrometallurgical processes. It terminates in a description of the Experimental Breeder Reactor II (EBR-II) Fuel Cycle Facility, in which pyrometallurgical processes will be used for the first time on an engineering scale for recovery of fuel discharged from the EBR-II. The operation of the Fuel Cycle Facility will be completely integrated with operation of the reactor. Recovered fuel, which will be refabricated in the Facility by remotely controlled equipment and processes, will be returned to the reactor. Because of the compactness of equipment, pyrometallurgical processes are believed to be particularly suited for use in small processing plants located on or near the reactor site; this concept is being evaluated in the EBR-II complex.

EBR-II Fuel Cycle Facility and Operations

The first fuel to be discharged from the EBR-II was successfully processed last September.[21] No additional fuel has been discharged from the reactor since that time.[22,23] Since early in October 1964, the reactor has been shut down for investigation and repair of two control rods and an oscillator rod which

were stuck.[22,23] Analyses of the purified ingot produced after melt-refining the first discharged material, which had received a burnup of 0.1%, showed the following removals of fission products: approximately 99% of the iodine and cerium, greater than 99.9% of the barium and lanthanum, and at least 99.99% of the cesium.[22] These are very good removals and are in accord with predictions based on small-scale experimental work.[24]

The bulk of the iodine, which, because of its short half-life, was present in nearly the maximum expected amount, was retained by a Fiberfrax fume trap,[22] a molded porous cup composed of amorphous alumina-silica fibers and inverted over the crucible. Some iodine and xenon were found in the oil of the vacuum pump by which gas is pumped from the melt-refining furnace to a holdup tank where it is stored for about one month before being discharged to the atmosphere. On the basis of these observations, it is expected that iodine release to the environment will be well below tolerance limits.

An 8-kg ingot (~93% yield) was obtained in processing the first active fuel in the EBR-II Fuel Cycle Facility.[22] This has now been processed through the first fuel-element refabrication operation, injection casting, in which molten fuel is forced by gas pressure into precision-bore (0.144-in. diameter) Vycor tube molds. Fuel-refabrication experience is also being gained by the reclamation of approximately 2500 fuel elements that had been prepared for dry and wet critical operations.[23] Two thousand elements have been made acceptable by sodium rebonding, and 350 have been remotely refabricated. Of the 2350 reclaimed fuel elements, 1673 have been made into reactor subassemblies.

When spent-fuel subassemblies are received from the EBR-II reactor, the outer sheath is cut and pulled off by a special machine and each of the exposed 91 fuel elements is then removed. The fuel-removal machine is an attachment to the subassembly dismantling machine and provides a remote, semiautomatic method for separating fuel elements from a subassembly. This machine was received, tested in the mockup area of the Fuel Cycle Facility, and then remotely installed on the dismantler.[22]

Graae has issued a report (Ref. 25) on the remotely removable and replaceable crane-bridge drive units of the EBR-II Fuel Cycle Facility. The drive units, which are designed to use a gear motor and an electromagnetic clutch, must be protected against high radiation and must operate satisfactorily in a very dry argon atmosphere. A novel pin-locating system was developed for precise installation of the drive unit by remote means.

Bernstein, Chilenskas, and Malecha have published the design of a 20-ton, portable, lead-shielded coffin for transport of fuel subassemblies between the EBR-II reactor and the adjoining Fuel Cycle Facility.[26] About 1 kw of heat can be removed from the fuel by a circulating gas stream and transferred to the lead shielding. Any sodium adhering to a spent subassembly may also be removed while the subassembly is in the coffin.

The volume of the Argon Cell of the Fuel Cycle Facility is 65,000 cu ft. The pressure control and purification systems for the argon atmosphere have operated very well since startup.[22] The air inleakage rate has been about 0.5 cu ft/hr. Water and oxygen concentrations have averaged 30 and 40 ppm, respectively. The high integrity of the Argon Cell and performance of the purification system are particularly noteworthy.

Although the concentrations of water and oxygen are maintained at low levels in the Argon Cell atmosphere, the concentration of nitrogen is allowed to build up to an equilibrium concentration of about 5 vol.%, depending on the inleakage rate of air and the rate of purging with high-purity argon. The effect of an argon–5% nitrogen atmosphere on various structural materials that are used at high temperatures is being investigated[23] as a result of a paper presented by Brunhouse (Ref. 27) in which he reported that pure nitrogen reacts with both Inconel 600 and Hastelloy X at a temperature of 950°C, thereby causing embrittlement of the alloy. Eight materials that may see service in the Argon Cell (Inconel 600 and 800, Hastelloy C and X, types 304 and 316 stainless steel, tungsten, and a molybdenum–30% tungsten alloy) have been exposed for 450 hr at 900°C to the argon–5% nitrogen atmosphere.[23] The Inconels and Hastelloys became less ductile but were still usable; the other materials were not significantly affected. Although these tests will continue until 2000 hr of exposure has been accumulated, it is doubtful that nitridation of these structural materials will be a serious

problem in the argon atmosphere of the EBR-II cell. Very little use of the high-nickel alloys at temperatures above 650°C is planned.

The high-purity inert atmospheres required for handling pyrophoric materials have adverse effects on equipment operation. Lubricants, for example, may lose their lubricity in a very dry atmosphere and thus cause bearing materials to wear rapidly. For this reason a large argon-atmosphere enclosure, 24 ft long by 14 ft high by 12 ft wide, is being installed[23] in the Chemical Engineering Division at Argonne, Ill., to determine the effects of a dry argon atmosphere on processes and equipment to be used in the EBR-II Cell.

Auxiliary EBR-II Fuel-Cycle Processes

Two auxiliary processes are required in the EBR-II fuel cycle: a process, known as the skull-reclamation process, for reclaiming melt-refining crucible residues and a process for concentrating plutonium that has been bred in the depleted uranium blanket of the EBR-II. Flow sheets of these processes were presented in previous issues of this journal (Refs. 28 and 29). The skull-reclamation process is under intensive development for installation in the EBR-II Fuel Cycle Facility. Little new information has been reported on the blanket process.

In brief outline the skull-reclamation process consists of oxidizing crucible residues to permit their removal from the crucible as a powder, mixing this powder into a molten-halide-salt mixture, and purifying the uranium by selective transfer of fission products or uranium between molten salt and molten zinc-magnesium solutions and by selective precipitation of uranium from metal solutions. The purification steps are all conducted in a single tungsten crucible and yield an intermediate product solution of uranium (10 to 12 wt.%) in a 12% magnesium–zinc solution. This solution is transferred to a tungsten crucible in a retort, where the solvent metals are vaporized away from the uranium. The recovered uranium is returned to the main fuel-processing stream by way of the melt-refining step.

The skull-reclamation process is currently being studied on an engineering scale (1.5 kg of uranium per charge), and prototype plant equipment is being developed. A problem of foaming in the molten-salt (flux) phase (47.5 mole % $CaCl_2$, 47.5 mole % $MgCl_2$, and 5 mole % CaF_2) has been encountered in several runs. This foaming was eliminated by careful pretreatment of molten flux with magnesium to remove any water present in the flux,[23] and the suspicion was thereby confirmed that foaming had been caused by reaction of magnesium and residual water in the flux to produce hydrogen.

Because of the hygroscopicity of the salt mixture used in the skull-reclamation process and the pyrophoric nature of the uranium product (which, after the retorting step, is hydrided to permit its removal as a powder from the tungsten crucible), plant-scale prototype equipment for the skull-reclamation process will be installed and tested[23] in the large argon-atmosphere enclosure that was described earlier.

Advanced Pyrometallurgical Processes

In progress at ANL is a fast breeder reactor study on a reference 1000-Mw(e) metal-fueled fast reactor to evaluate its thermal, neutronic, and economic performance.[23] The analysis is based on an average fuel burnup of 5.5% of the uranium and plutonium in a uranium–18 wt.% plutonium–5 wt.% fissium fuel clad in a vanadium–20% titanium alloy. The conceptual fuel cycle is, in many respects, similar to the EBR-II fuel cycle. However, halide slagging was substituted for melt refining for processing core material. In halide slagging, a procedure described in a previous Review,[30] electropositive fission-product elements such as the rare earths and alkaline earths are selectively oxidized and extracted from the molten core alloy into an overlying halide-salt flux.

In halide-slagging studies now under way at ANL, the equilibrium of rare earths and plutonium between molten uranium-plutonium-fissium alloys and molten salts is being investigated.[22,23] It is possible that this procedure may be employed to selectively extract plutonium from blanket material. An attempt to remove zirconium from a molten core alloy by oxidation with magnesium chloride to the tetrachloride was unsuccessful.[22] Although the available free-energy data indicate that this oxidation should not proceed to an appreciable extent, it was hoped that the reaction would be driven by continuous distillation of magnesium and $ZrCl_4$.

In other advanced processes under development at ANL, the fuel material is dissolved in

a molten-metal solvent such as cadmium or zinc. Then the fission-product purification is achieved by selective extractions between molten-metal and halide-salt phases that are caused by selective oxidation or reduction reactions. A typical flow sheet was given in Ref. 31. It is presently assumed that the core alloy will be clad with a vanadium–20 wt.% titanium alloy. Various methods of chemically separating the fuel alloy from the cladding are being investigated. An HF-oxygen mixture at 500°C did not react selectively with the cladding as hoped but oxidized the fuel as well.[22] This approach has been discontinued. Another approach is based on the permeability of the cladding to hydrogen.[23] As the fuel reacts with hydrogen, it expands and fragments the cladding. The fuel would later be dehydrided and selectively dissolved in liquid-metal solvent. The solution would then be separated from the insoluble cladding.

In the molten-salt processes, rare earths are extracted into the salt phase, which has the composition: 30 mole % NaCl–20 mole % KCl–50 mole % $MgCl_2$. To permit recycle of the salt as well as consolidation of the fission products into compact shapes for disposal or, possibly, utilization as power sources, investigators studied the extraction of fission products from the salt into various magnesium alloys. Distribution coefficients (concentrations in salt/concentrations in metal) of praseodymium and lanthanum between the salt mixture and aluminum-magnesium alloys were found to be as low as 4.3×10^{-4} and 3×10^{-3}, respectively.[22,23] The solubilities of the rare-earth elements in aluminum-magnesium alloys are rather high and reach values of several percent in the temperature range of 550 to 900°C. These solubility values, in conjunction with the favorable distribution coefficients, should permit the preparation of highly concentrated waste alloys.[23]

Less favorable distribution of rare earths into the metal phase prevailed with antimony-magnesium alloys, whereas with copper-magnesium alloys, praseodymium distributed strongly to the salt phase.[22] In fact, in the copper-magnesium-salt system, a plutonium-praseodymium separation factor of at least 240 can be achieved.[22] Consequently this system may be attractive for separation of rare earths from plutonium.

The potential of metal-salt systems for separating rare-earth elements and yttrium from transplutonium elements has also been studied.[22] Yttrium was employed in these studies since previous work[32] showed that it could be one of the most difficult of the above fission-product elements to separate from certain transplutonium elements. Distribution data shown in Fig. III-5 indicate that reasonably

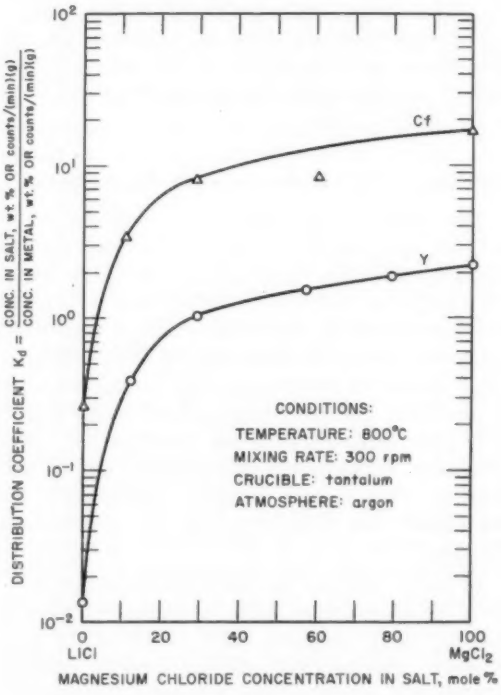

Fig. III-5 Distribution of californium and yttrium between zinc–6 wt. % magnesium and LiCl-$MgCl_2$ salt.[22]

good separation of californium from yttrium could be achieved with a zinc–6 wt.% magnesium alloy and LiCl-$MgCl_2$ salt mixtures.[22]

Preparation of Metals by Reduction of Their Compounds

Related to process steps employed in pyrometallurgical processes are the processes employed for winning metals from their compounds. In this connection attention is directed to four electrolytic processes for purifying or recovering metals used in nuclear programs:

1. Continuous electrowinning of cerium from cerium oxides[33]
2. Molten-salt electrorefining of uranium[34]
3. Phenomenon of iron concentration in the vicinity of a cathode during electrorefining of uranium in a molten-salt bath[35]
4. Fused-salt electrorefining of plutonium and its alloys[36]

Fundamental Studies Relative to Liquid-Metal-Process Development

The logical design of pyrometallurgical processes requires the development of a broad base of fundamental information. A significant quantity of thermodynamic data is now available on the metallic systems of the fissionable metals, plutonium, thorium, and uranium. Because some of these data are scattered throughout various AEC reports and hence are not readily available, Johnson has collected and critically evaluated the data[37] available through 1963. The result is a very worthwhile compilation that can be used not only for process-development purposes but also for meaningful estimations of thermodynamic data in other systems and at conditions outside those used in the original experiments.

Johnson and Chasanov have also published an article on the thermodynamics of the plutonium-zinc system.[38] Zinc is a solvent in many pyrometallurgical processes, and so the information is timely. Thermodynamic data for the zinc-rich plutonium compound ($PuZn_{12}$) are compared in Table III-3 with data for the zinc-rich compounds of uranium and thorium. The enthalpies and entropies are among the most negative reported for metallic systems, a fact that the authors state cannot be explained in terms of order-disorder phenomena, but most originate from significant differences between the vibrational, electronic, and magnetic properties of the compounds and their pure constituents.[38]

The phase diagram of the plutonium-zinc system, previously reviewed as a TID report, has now been published[39] in a journal article. Also of interest for process applications is the plutonium-magnesium system. An immiscibility gap in this system has been defined in recent experiments[22] (see Fig. III-6). The region of liquid immiscibility extends from about 8.5 to 84 at.% magnesium at 625°C; the consolute temperature is about 975°C. Phase relations in the plutonium-cerium system, alloys of which are of interest as reactor fuels, have recently been determined by Selle and Etter.[40]

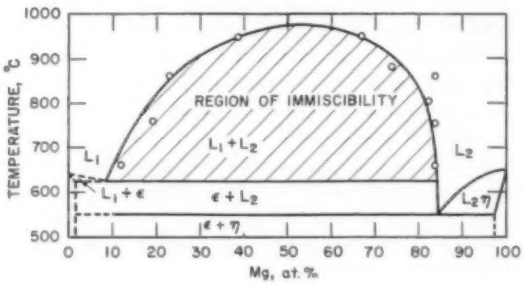

Fig. III-6 Liquid-immiscibility gap in the magnesium-plutonium binary system.[22]

Coprecipitation is an important phenomenon in processes in which fractional crystallization is employed as a purification method. Moriarty, Johnson, and Feder have studied this phenomenon[41] by measuring the substitutional carrying of trace metals with $CeCd_{11}$ as it is precipitated from liquid cadmium. The Doerner-Hoskins logarithmic distribution law was found to apply in all cases (see Fig. III-7). Coprecipitation was most extensive for those tracer metals

Table III-3 THERMODYNAMIC QUANTITIES OF ACTINIDE-METAL–ZINC COMPOUNDS[38]

(Mean Values over Temperature Range 500 to 700°C)

Compound	$\Delta Hf°$, cal/gram atom*	$\Delta Sf°$, cal/(deg)(gram atom)*	ΔHf,† cal/gram atom*	ΔSf,† cal/(deg)(gram atom)*
$\frac{1}{2}Th_2Zn_{17}$	−48,100‡	−33.5‡	−33,100	−11.8
UZn_{12}	−54,200§	−38.2§	−33,000	− 7.6
$PuZn_{12}$	−75,300	−45.7	−54,100	−15.1

*Of the actinide metal.
†Formation from solid zinc.
‡P. Chiotti and K. J. Gill, *Trans. AIME*, 221: 573 (1961).
§I. Johnson and H. M. Feder, *Thermodynamics of Nuclear Materials*, p. 319, International Atomic Energy Agency, Vienna, 1962.

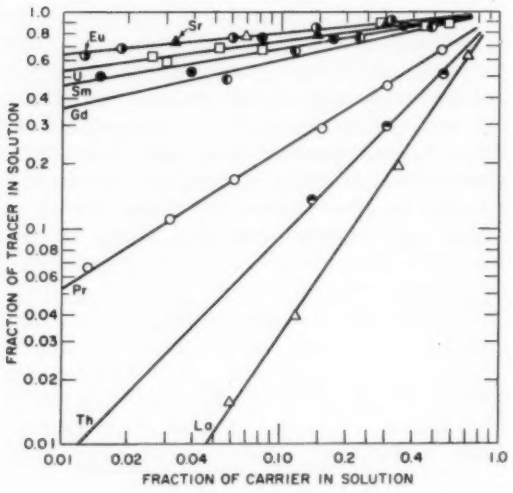

Fig. III-7 Coprecipitation of tracers with $CeCd_{11}$ from liquid cadmium.[41]

which form an intermetallic compound isostructural with, or closely related to, $CeCd_{11}$.

Construction Materials for Liquid-Metal-Fuel or Liquid-Metal-Process Systems

Cash, Fisher, and Core of Ames Laboratory have evaluated[42] various materials (niobium, tantalum, yttrium, and Inconel) for containing molten aluminum, bismuth, lead, tin, and zinc and their respective uranium and thorium alloys. All corrosion tests were made under static, isothermal conditions in small capsules. Overall, the best container material was tantalum, followed in order by niobium, Inconel, and yttrium. However, the report should be consulted to determine corrosion by specific systems. Combinations of liquid fuel alloys and container materials that showed promise were uranium-lead or thorium-lead alloys in tantalum or niobium and a uranium-bismuth-tin alloy in tantalum. Various corrosion mechanisms were elucidated, and methods of inhibiting corrosion were suggested.

Miscellaneous

Bunshah[43] of the Lawrence Radiation Laboratory has reported on a theoretical study of "superpurification" of metals by vacuum distillation. The most important factors in the production of very high-purity metals by distillation are: (1) high evaporation rate, (2) minimum contamination from vacuum environment, (3) good control of condensation temperature, (4) high-quality starting material, and (5) elimination of melt-crucible reactions.

Cahill and Grosse[44] at the Philadelphia Research Institute have published a sixth annual report on basic research in inorganic and physical chemistry at high temperatures. The topics discussed include: (1) description of an oscillating crucible viscosimeter, (2) surface-tension measurements of liquid uranium, UF_4, and ThF_4, (3) measurements of density of beryllium and antimony, (4) interactions of materials at high temperatures, and (5) a very noteworthy achievement, the formation of a ThO_2 liquid crucible* that, in principle, makes it possible to contain liquids on ThO_2 at temperatures up to its boiling point (~4670°K).

Grosse has also developed a relation that empirically relates the surface tension and energy of liquid metals with their heat of vaporization at the melting point.[45] He demonstrated that the free surface energy† of metals at their melting point equals 15% of their heat of vaporization at the melting point.

Levinson[46] of the Los Alamos Scientific Laboratory has determined the heat content of gamma uranium between 1205 and 1394°K with a drop calorimeter. For gamma uranium:

$$H_T - H_{310°K} = (9.581T - 1757) \text{ cal/mole}$$

with a standard deviation of 5.94 cal/mole. F molten uranium:

$$H_T - H_{310°K} = (11.45T - 2395) \text{ cal/mole}$$

with a standard deviation of 27.54 cal/mole. The specific heats were 9.58 cal/(mole)(°K) for gamma uranium and 11.45 cal/(mole)(°K) for molten uranium. The heat of fusion was found to be 1990 ± 130 cal/mole. (L. Burris, Jr.)

Other Nonaqueous Processes

Pyrochemical processes that employ dry, high-temperature chemical conversions are be-

*A stable liquid pipe or tube of thoria formed by melting a solid thoria pipe in a helium plasma stream.

†Product of surface tension times true atomic surface area at the melting point.

ing developed for the recovery of fissile and fertile material from irradiated oxide and carbide fuels. Gases and molten salts are generally used as reagents and process media. These relatively simple, low-decontamination processes, coupled with remote fuel-refabrication procedures, are particularly suited to the rapid recycle of short-cooled high-burnup fuels.

Oxide Fuel Processing

Research and development studies have continued at Hanford[47–49] on the salt-cycle process, a pyrochemical procedure for processing mixed UO_2-PuO_2 fuels for recycle to thermal heterogeneous reactors. In the salt-cycle process, vibratory decladding is used to remove the irradiated UO_2-PuO_2 fuel from the Zircaloy cladding, the UO_2 is then oxidized to U_3O_8, and the resulting mixture of powdered U_3O_8 and PuO_2 is dissolved in a molten salt such as LiCl-KCl by sparging the system with gaseous chlorine and HCl. A plutonium-uranium separation can be effected by (1) chemically precipitating uranium-free PuO_2 by sparging the melt with an oxygen-chlorine mixture or (2) electrodepositing plutonium-free UO_2 on a graphite cathode and subsequently codepositing a UO_2-PuO_2 mixture that is enriched in plutonium. The salt-cycle-process flow sheet was described in greater detail in the preceding issue of *Reactor Fuel Processing*.[50]

In continuing engineering-development studies of the salt-cycle process, about 15 lb of mixed oxide was successfully removed from five Zircaloy-clad cold-swaged half fuel rods prepared by bisecting rods that had been irradiated to 5000 Mwd/metric ton in the Plutonium Recycle Test Reactor.[47,49] The cladding showed no signs of embrittlement, and there appeared to be no release of radioactive dust to the cell atmosphere. The Zircaloy was sectioned and leached with 16*M* HNO_3 to determine uranium and plutonium losses in the waste cladding. The uranium loss varied from 0.5% at the open end to 0.65% near the closed end of the half rod, and the average plutonium loss was about 0.8%. In some instances about 2.5% of the total uranium remained near the closed end of the rod where the air hammer could not be operated effectively. The uranium and plutonium losses for the irradiated fuel, although not large, were somewhat higher than the value of less than 0.1% that had been obtained previously in the decladding of unirradiated mixed oxides.

Other engineering studies have been conducted on the precipitation of PuO_2 from molten chlorides.[48] Sparging a LiCl-KCl salt bath (mole ratio 1 : 1) containing dissolved uranium and plutonium with pure oxygen resulted in precipitation of 92% of the plutonium initially present in the solution. The following percentages of fission-product elements were precipitated with the plutonium: ^{144}Ce, 92%; ^{91}Y, 18%; ^{147}Pm, 5%; and ^{154}Eu, 2%.

Laboratory studies of the chemical precipitation of PuO_2 in the salt-cycle process have indicated that over 99.7% recovery of plutonium from the salt can be effected by a two-step procedure.[48] When a LiCl-KCl melt (mole ratio 2.5 : 1) containing dissolved uranium and plutonium was sparged with an oxygen-chlorine stream at 575°C, 95% of the plutonium was precipitated as PuO_2. Upon additional sparging with a hydrogen-argon mixture, the remainder of the plutonium was precipitated as PuO_2 and about 5% of the uranium was precipitated as UO_2.

Further studies were conducted in which variations were made in the compositions of the molten salt and the sparge gases and in the duration of treatment.[49] With melts initially containing about 20 wt.% of uranium and 0.2 wt.% plutonium, and at an operating temperature of 575°C, the following results were obtained:

1. In a LiCl-KCl melt (mole ratio 2.5 : 1) sparged with 20% oxygen–80% chlorine for 3 hr and then with 8% hydrogen–92% argon for 0.5 hr, 99.6% of the plutonium was precipitated. Decontamination factors for uranium and neodymium (a representative rare-earth fission product) were 700 and 110, respectively. The rare-earth decontamination factor decreased with an increasing oxygen-to-chlorine ratio in the sparge gas.

2. In a LiCl-KCl melt (mole ratio 1 : 1), precipitation of plutonium was essentially complete, but the rare-earth decontamination factor was only about 40.

3. Use of 100% argon in the second phase of the sparging procedure produced essentially complete precipitation of the plutonium by sweeping out dissolved chlorine and oxygen, thereby allowing the soluble plutonyl ions to decompose thermally to PuO_2. With pure argon, however, reaction was slow and the rare-earth decontamination factor was low.

Additional spectrophotometric observations have been made on the behavior of plutonium dissolved in chloride melts.[48] Studies with LiCl-KCl (mole ratio 3:1) showed that this solvent exhibits less complexing strength than those observed earlier: LiCl-KCl (mole ratio 1.4:1), LiCl-KCl (mole ratio 1:1), and LiCl-CsCl (mole ratio 1.4:1). The molar ratio, R, of Pu(IV) to Pu(III) in the chlorine-saturated melt was about four-tenths of that in LiCl-CsCl (1.4:1). The ratio, R, in LiCl-KCl (3:1) from 500 to 700°C can be expressed as

$$\log R = \frac{2660}{T} - 3.77$$

About 32% of the plutonium is present as Pu(IV) at 500°C and about 8% at 700°C. The ratio of plutonyl(VI) to plutonyl(V) in the LiCl-KCl (3:1) melt sparged with an oxygen-chlorine mixture was also lower than the ratios observed in the salt systems that had been studied earlier.[48] Plutonyl(V) ion was the predominant plutonium species in the solution. The following equilibrium reaction was studied to determine how low a plutonium concentration might be achieved through the precipitation of PuO_2 by oxygen-chlorine sparging:

$$PuO_2 + \tfrac{1}{2}Cl_2 \rightleftharpoons PuO_2Cl$$

At 600°C the limiting plutonium concentration in the salt may be expressed as

$$\text{Wt.\% Pu} = 0.028\ (X_{Cl_2})^{0.5}$$

where X_{Cl_2} is the mole fraction of chlorine in the sparge gas. The temperature coefficient of the equilibrium has not yet been determined. The rate of approach to equilibrium appeared to be relatively slow, with about 5 hr required to reach a steady equilibrium value.

Investigations have been started on the electrochemical behavior of noble-metal and rare-earth ions in salt solutions.[48] In a study of noble-metal microelectrodes, gold and platinum exhibited some differences in behavior. Electrode-potential data obtained with nonporous graphite electrodes for $5 \times 10^{-3} M$ solutions of ruthenium, rhodium, and palladium in LiCl-KCl melts indicated that these elements will codeposit with UO_2 in the uranium electrodeposition step of the salt-cycle process. The results also indicated that it is unlikely that a satisfactory uranium–noble-metal separation can be achieved through prior electrodeposition of noble metals before the uranium-electrodeposition step. On the other hand, at temperatures above 700°C, ruthenium, rhodium, and palladium were precipitated from melts containing dissolved ions of these metals. Precipitation at lower temperatures also occurred upon exposure of the melt to oxygen or upon the addition of Li_2CO_3. Electrochemical studies of the rare-earth elements were complicated by electrode difficulties. Neodymium and samarium oxides, however, were precipitated by the addition of carbonate to the chloride melt. The precipitated oxides were readily redissolved by sparging the melt with HCl gas.

Work is also in progress at Hanford on methods for the determination of oxygen-to-uranium ratios in UO_2-containing materials.[49] The first technique to be examined consists in reducing hyperstoichiometric UO_{2+x} to UO_2 with a gas such as hydrogen or CO and measuring the gaseous reaction products. Preliminary results of this procedure have been encouraging.

Conversion of Fluorides to Oxides in Molten-Salt Media

Investigators at CEN, Mol, Belgium, are studying the conversion of uranium and plutonium fluorides to the oxides by means of reactions in molten-chloride media.[8–11] This procedure is being developed for the purpose of reconverting the products of fluoride-volatility processes to oxides for recycle to oxide-fueled reactors. (See page 93 for a discussion of the fluoride-volatility processes.) The chemical reactions on which the procedure is based, however, are essentially the same as those involved in the Hanford salt-cycle process.

The first step of the procedure consists of absorbing or dissolving fluorides of uranium and plutonium (UF_4, UF_6, PuF_4, PuF_6) in a molten-chloride-salt mixture such as NaCl-KCl or LiCl. Sparging of the salt with an oxygen-containing gas (an oxygen-HCl mixture, for example) permits plutonium to be precipitated from the solution as PuO_2, but uranium remains in the solution as uranyl ion. The uranium can then be recovered in a later step either by electrodeposition of UO_2 on a graphite cathode or by chemical precipitation of UO_2 through hydrogen sparging.[11]

In studies of the reconversion of UF_6 to UO_2, approximately 70 g of UF_6 was added to 900 g of LiCl-KCl eutectic (59 mole % LiCl–41 mole %

KCl) at 450°C by introducing UF_6 vapor into a warm nitrogen stream and bubbling the gaseous mixture through the melt.[8–10] Chemical analyses of the salt solution showed that most of the uranium was in the tetravalent state. The excess fluoride apparently became fixed in the salt as alkali fluorides, with the evolution of gaseous chlorine:

$$UF_6 + LiCl + KCl \rightarrow UF_4 + LiF + KF + Cl_2\uparrow$$

The absorption of UF_6 was much more efficient when the chloride melt contained some moisture than it was with dried melts.

Treatment of the melt with HCl gas to avoid excessive buildup of the fluoride content has been investigated. Conversion of alkali-metal fluoride, MF, to the chloride occurs by the following reaction:

$$MF + HCl \rightarrow MCl + HF\uparrow$$

Thermogravimetric measurements showed that at 700°C, 70% of LiF, 90% of KF, and 95% of NaF are reconverted to the chlorides by the HCl treatment.[10]

Several additional experiments were performed to determine the efficiency of UF_6 absorption by a chloride melt and to examine the influence of moisture in the salt on the nature of UO_2 obtained by electroreduction.[10] The conditions and results of the experiments are summarized in Table III-4. In each experiment UF_6 vapor in a nitrogen stream was injected into 300 g of LiCl-KCl eutectic (59 mole % LiCl–41 mole % KCl) at 500°C under an air atmosphere. Quartz apparatus was used. Provisions were made to sparge the melt with air or oxygen saturated with water at room temperature, and in one experiment, B1.14, the air was saturated at 65°C. After the UF_6 absorption step, the melt was dehydrated by sparging with chlorine or HCl gas for 1½ hr at 500°C; then the dissolved uranium was electrodeposited on a graphite cathode. Under these conditions the percentage of UF_6 absorbed by the melt was rather low (38 to 44%). In run B1.16, in which the air sparge was replaced by moist oxygen and the UF_6 was dispersed in the center of the melt through a perforated sphere, 70.5% of the UF_6 was absorbed. The oxygen-to-uranium ratio of the UO_2 products was slightly in excess of the theoretical value of 2.000.

Three additional experiments[10] to determine the effect of moisture in the melt on the absorption of UF_6 are listed in Table III-5. The

Table III-4 ABSORPTION OF UF_6 BY LiCl-KCl EUTECTIC AND ELECTROLYTIC REDUCTION OF THE PRODUCT[10]

Experiment	B1.12	B1.13	B1.14	B1.15	B1.16
Quantity of UF_6 used, g	20	21	21	60	50
Percentage of UF_6 absorbed	Not determined	38	44	44	70.5
Oxidation					
Gas	Damp air	Damp air	Damp air	Damp N_2, damp O_2	Damp O_2
Flow, liters/hr	45	45	45	45	45
Drying					
Gas	HCl	HCl	HCl	Cl_2	HCl
Flow, liters/hr	54	54	54	54	54
Time, min	90	90	90	90	90
Electrolysis					
Initial potential, volts	1.95	1.9	1.9	1.9	1.8
Final potential, volts	1.8	1.9	1.8	1.8	1.95
Initial current strength, amp	0.7	0.5	0.4	1	0.7
Final current strength, amp	0.35	0.17	0.35	0.2	0.15
Electrolysis time, min	110	125	160	225	660
Electrolytic efficiency, %	71.8	78	83	78	73
UO_2 product					
UO_2 collected, g	4.3	5	6	14	25
UO_2 adherence to cathode	Bad	Bad	Bad	Good	Very good
Oxygen-to-uranium ratio	2.013	2.005	2.004	2.004	2.022
Crystal form	Fine powder	Fine powder	Fine powder	Well-formed cubic crystals	Well-formed cubic crystals
Impurities					
Li^+, ppm	650	120	90	200	120
Na^+, ppm	1350	630	700	140	280
K^+, ppm	390	150	100	340	165

Table III-5 ABSORPTION OF UF_6 BY DRIED AND UNDRIED LiCl-KCl EUTECTIC[10] AT 500°C

Experiment	B1.17	B1.18	B1.19
Drying of the bath			
Gas and flow	HCl, 55 liters/hr	Not dried	HCl, 55 liters/hr
Time, min	30		60
Absorption of UF_6			
Quantity, g, of UF_6 used in 300 g of eutectic	40	70	61
Percentage of UF_6 dissolved	69	91.5	51.6
Percentage of U^{4+} dissolved	64	83	80
Percentage of U^{6+} dissolved	36	17	20

LiCl-KCl eutectic was used at a temperature of 500°C. Two runs in which the melt was dried by sparging with HCl gas resulted in the absorption of 51.6 and 69% of the UF_6. In a third run, in which the melt was not dried, 91.5% of the UF_6 was absorbed. In all three of the runs, the major fraction of the uranium in solution was in the tetravalent state, with the remainder in the hexavalent state.

The conversion of UF_4 and mixtures of UF_4 and PuF_4 to oxides in molten-chloride media was also investigated at CEN.[8,9] In one experiment a 25-g charge of UF_4 was added to 300 g of predried LiCl-KCl eutectic, the melt was oxidized at 500°C by sparging 2 hr with an oxygen-HCl mixture, and then the system was sparged with HCl gas for 40 min. The solution was electrolyzed at 500°C with HCl sparging, and graphite electrodes were used for the anode and cathode. A UO_2 product was obtained, with oxygen-to-uranium ratios ranging from 2.0013 to 2.0050. Experiments were also reported in which UF_4-PuF_4 mixtures (6:1 by weight) were added to the LiCl-KCl eutectic and the system was sparged with an oxygen-chlorine mixture at 550 to 560°C. The salt solution showed a yellowish-orange color characteristic of uranyl(VI) ion, and solid PuO_2 was precipitated on the walls of the vessel. In the final experiment the solubility of plutonium in the melt under these conditions was 0.24 g per kilogram of salt. These results indicate that separate recovery of PuO_2 and UO_2 from the molten-chloride solutions may be feasible.

Carbide Fuel Processing

Three reports (Refs. 51 to 53) have been issued by Atomics International on the processing of UC fuels by the nitride-carbide cycle. This process consists in three basic steps: (1) reaction of the UC fuel with nitrogen at 750 to 950°C to form a pulverized mixture of uranium nitride (U_2N_3) and carbon, (2) reconversion of this mixture to UC by heating in vacuum at 1300 to 2100°C, and (3) arc melting to consolidate the reconverted carbide and to remove residual nitrogen.

The first (Ref. 51) of the three reports, which deals with the kinetics of nitride formation (step 1 of the process), was reviewed in the Spring 1964 issue of *Reactor Fuel Processing*.[54] The second report (Ref. 52) is concerned with the kinetics of the reconversion step, i.e., the reaction of U_2N_3 with carbon. A thermogravimetric balance was used to measure the reaction rates over a temperature range of 950 to 1300°C at pressures below 10 μ. The rate data, together with chemical analyses and X-ray results from samples of the products, indicated that the reconversion proceeds by a two-step reaction:

$$U_2N_3 + 2C \rightarrow 2UN + 2C + \tfrac{1}{2}N_2\uparrow$$

$$2UN + 2C \rightarrow 2UC + N_2\uparrow$$

The first reaction represents the thermal decomposition of U_2N_3 in the presence of carbon, and the second reaction represents the reconversion of nitride to carbide. The reaction rates were expressed by an equation of the general form

$$W = kt^n$$

where W = weight loss of the sample, mg
k = rate constant
t = time, min
n = constant that is characteristic of the rate law that prevails

The rate for the thermal decomposition of U_2N_3 in the presence of carbon was linear. For the Arrhenius expression

$$\ln k = \frac{-\Delta E}{RT} + \ln A$$

the ΔE value (activation energy) was 90.6 ± 11.8 kcal/mole, and the average value of ln A (A is the frequency factor) was 32.0.

For comparison the thermal decomposition rate of U_2N_3 in the absence of carbon was also determined.[52] The decomposition began at about 650°C, and at 1000°C 2 to 3 hr was required for complete conversion of the U_2N_3 to UN. Although it was not possible to fit a simple rate equation to the data over the entire decomposition range, a linear rate law was applicable to the initial stage of the reaction. The observed activation energy was 64.6 ± 7.7 kcal/mole. Comparison of the U_2N_3 thermal decomposition rates in the presence and absence of carbon suggests that the reaction is impeded by the presence of carbon.

The reconversion of UN to UC was investigated from room temperature[52] to 1645°C. Nitrogen evolution began to occur at about 1040°C, and the rate of the reaction increased with rising temperature. The data were fitted most closely by a parabolic rate law

$$W = kt^{1/2}$$

which is characteristic of a diffusion-controlled process. The activation energy was 31.3 ± 1.1 kcal/mole, and the average value of ln A was 11.9. Thus the rates of the two steps of the nitride reconversion reaction may be expressed as

1. Thermal decomposition:

$$\ln k = 32.0 - (45{,}600/T)$$

2. Reconversion:

$$\ln k = 11.9 - (15{,}750/T)$$

The third report (Ref. 53) of the series on the nitride-carbide process describes laboratory-scale studies of the effects of recycling fuel through the process and investigations of the behavior of fission products. Two nitriding-reconversion recycle experiments were performed, one through 3 cycles and the other through $2\frac{1}{2}$ cycles. The experimental procedure used in the recycle experiments consisted in heating a 10-g UC sample under vacuum in a molybdenum vessel and then adding nitrogen to the system at various pressures for different periods of time. The U_2N_3 product was then reconverted to UC by evacuating the system, heating rapidly to 800°C, heating to 1300°C at a rate of 100°C/hr, and finally heating to the maximum temperature at 250°C/hr. Arc melting was then employed to consolidate 5 to 6 g of the product into buttons.

The physical characteristics of the products of these process steps are shown in Fig. III-8. The granular UC used as the starting material

Fig. III-8 Material phases in the nitride-carbide processing cycle.[53]

was thoroughly pulverized by the nitriding treatment, and the powdered mixture of U_2N_3 and carbon was sufficiently homogeneous that mixing was not required prior to the reconversion step. Nitridation at a lower temperature (750°C) was slower but produced a finer powder than a higher temperature reaction (950°C). In the reconversion step the nitrided product was heated in vacuum from 1300 to 2100°C in various crucible materials. Heating to 1650°C resulted in a residual nitrogen content of less than 0.3 wt.%. At 1850°C, less than 0.1 wt.% nitrogen remained, and, at 1950°C and above, nitrogen removal was essentially complete. All the reconversion products were porous sintered compacts, and the products from reactions above 2000°C were slightly fused. Photomicrographs showed the product to be UC. Small amounts of nitrogen could apparently be substituted for carbon without disturbing the UC lattice and probably without adverse effects on the fuel. Materials reported to be suitable as containers for the reaction above 1700°C were tungsten, tungsten carbide, and graphite.

The behavior of fission products in the nitride-carbide process was investigated in six experiments with 10 to 11 g of UC that had been irradiated to 10^{17} neutrons/cm^2 and cooled approximately one year.[53] In the nitriding step the UC was exposed to 0.95 atm of nitrogen for 6 to 7 hr at 750 to 950°C. No fission-product removal occurred in this step. Reconversion of the nitride was effected by heating the U_2N_3-carbon mixture under vacuum for 1 to 5 hr at 1700, 1850, or 1950°C. The degree of fission-product removal in the reconversion step increased with higher temperatures and longer heating periods. In general, fission-product removals in this step were approximately as follows: cesium and strontium, approximately 95%; rare earths, 50%; cerium, 20 to 60%; zirconium and niobium, minor amounts. Significant plutonium losses (~40%) occurred upon heating at 1850 and 1950°C.

Overall fission-product removals for the combined nitriding, reconversion, and arc-melting steps are listed in Table III-6. About 75% removal of the gross beta activity from the UC fuel can apparently be expected in the complete cycle. (R. K. Steunenberg)

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Table III-6 FISSION-PRODUCT REMOVAL IN THE NITRIDE-CARBIDE CYCLE INCLUDING ARC MELTING[53]

Run No.	Time liquid, min	Product composition		Percent removal							
		Nitrogen, wt.%	Carbon, wt.%	Gross beta	Cs	Ce	Sr	Zr-Nb	Ru	Pu	Rare earths (less Ce)
1	6	0.009	5.20	85	>99	87	>99	36	27	84	95
2	2	0.030	4.75	69	>99	64	>99	15	17	65	85
3	2	0.008	5.55	70	>99	70	>99	42	22	66	86
4	6	0.008	5.25	77	>99	82	>99	40		78	92
5	2	0.007	6.60	61	>99	60	>99	41	30	53	70
6	6	0.005	6.45	73	>99	73	>99	31	31	72	84

*Each sample was approximately 6 g of powder.

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Section

IV

Reactor Fuel Processing

Waste Disposal

Treatment of Liquid Wastes by Foam Separation and Freeze Drying

Oak Ridge National Laboratory (ORNL) is continuing its plans for a pilot-plant demonstration of a scavenging-precipitation foam-separation process for removing ^{90}Sr from ORNL low-level-activity waste (LAW).[1,2] The process involves two steps: (1) a precipitation and coagulation head-end step in which calcium and magnesium hardness ions are precipitated, the interference effect of phosphates is reduced, and clarification follows in an upflow sludge-bed filter; and (2) a foam-separation procedure removes the ^{90}Sr. The latter step is carried out in a countercurrent foam contactor. The design of the countercurrent foam contactor and the associated surfactant recovery columns has been completed, and the system is being built.[2] The contactor (Fig. IV-1) is 24 in. square and has approximately 8 ft of countercurrent contacting height. Feed enters the top of the primary foam column and passes down counter to the foam bubbles. Foam leaving the drying section is collapsed in a centrifugal foam breaker. Treated liquid from the bottom of the column is fed continuously to the recovery columns that are adjacent to the countercurrent column. These columns comprise a series of three 24-in.-square columns where the surfactant is stripped and then recycled back to the bottom of the countercurrent column.

Air that is separated from the foam in the centrifugal foam breaker is split into three equal streams and fed to the foam sections of each recovery column through auxiliary air-inlet nozzles. This helps to remove the foam quickly before collapse can occur. Air leaving the orifice foam breakers is recycled to spinnerets and spargers in the four columns.

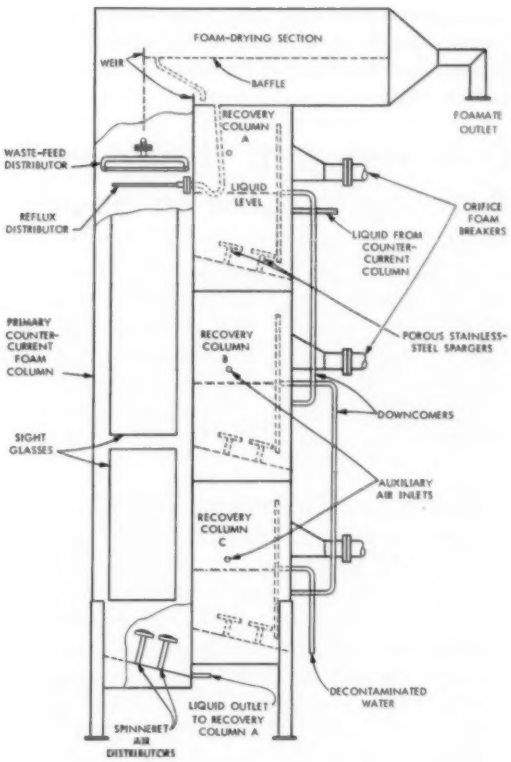


Fig. IV-1 Foam columns: low-level pilot plant.[2]

Freeze Drying

French workers at Saclay have been investigating a freeze-drying method for the treatment of intermediate-level-activity wastes.[3,4] The method involves the desiccation of frozen material at low temperature under vacuum and

yields a residue that is a dry, powdery substance. The process, because of the low temperatures, is expected to prevent the loss of volatile elements such as ruthenium, to minimize corrosion, and to result in high decontamination factors ($\sim 10^6$). Laboratory experiments were made with low-level-activity solutions (10^{-3} to 10^{-5} curie/liter). The freezing step was carried out at $-40°C$ and the sublimation step, at 30°C under a vacuum of 10^{-1} to 10^{-2} mm Hg pressure. Decontamination factors approaching 10^6 were obtained. A pilot plant capable of handling 4 m^3 of radioactive wastes per day (up to 10 curies/m^3) is under construction.

Conversion of High-Level-Activity Wastes to Solids

Proceedings (Ref. 5) have become available of the fourth working meeting on the calcination and/or fixation of high-level-activity wastes in stable, solid media. The meeting was held Feb. 11 and 12, 1964, at Brookhaven National Laboratory (BNL). Status reports were presented on the research, development, and demonstration programs being carried out at various sites in the United States. The following programs were discussed:

1. Fluid-bed calcination process, Idaho Chemical Processing Plant (ICPP)
2. Phosphate-glass process, BNL
3. Potcal process (conversion to calcined solids in a pot) and potglass process (conversion to a glassy solid by addition of glass-forming materials), ORNL
4. Radiant-heat spray-calcination and pot-calcination processes and plant-level-activity waste demonstrations of selected solidification process, Hanford Laboratories

At Hanford the phosphate-glass, pot-calcination, and radiant-heat spray-calcination processes are scheduled for pilot-plant demonstration during 1965 with actual high-level-activity liquid wastes.[6] Prototype demonstration equipment, referred to as waste-solidification engineering prototypes, for each of the processes is being designed and fabricated. Information needed for the design, development, and operation of prototype equipment is being obtained on a national cooperative program in which BNL, ORNL, and Hanford are involved. A simplified flow diagram of the waste-solidification engineering prototypes is shown in Fig. IV-2.

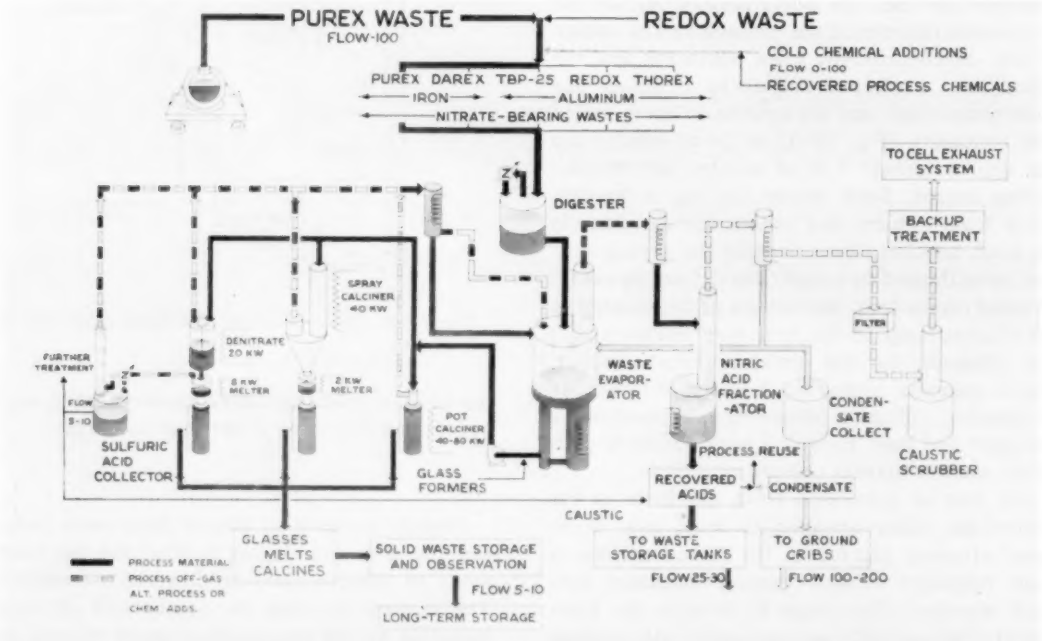


Fig. IV-2 Waste-solidification engineering prototypes.[5]

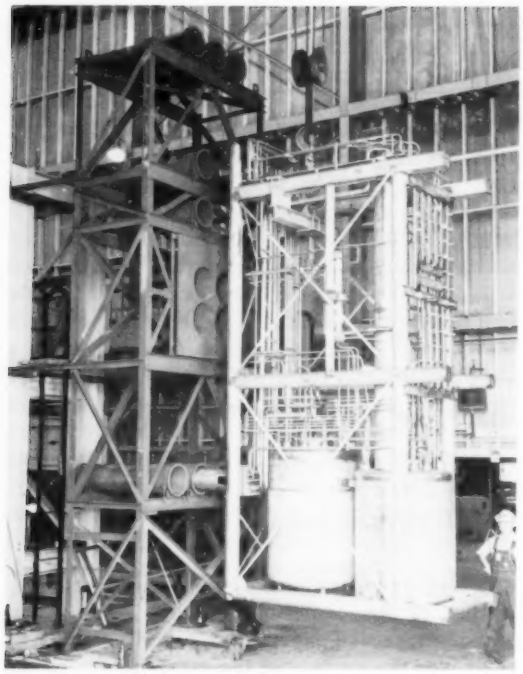


Fig. IV-3 Waste-solidification engineering prototype rack.[5]

Flexibility in the operation of the facility is made possible by the use of (1) remotely removable modules or racks (see Fig. IV-3) on which associated pieces of equipment are grouped, thereby facilitating maintenance and modification, and (2) auxiliary equipment (e.g., feed preparation and off-gas treatment) that is common to all the solidification-equipment concepts.

Fluid-Bed Calcination

The fluid-bed calcination process has been successfully demonstrated in the 60 gal/hr Waste Calcining Facility (WCF) at the National Reactor Testing Station (NRTS).[7] The first run using high-level-activity liquid wastes from the ICPP was terminated, as scheduled,[8] during October 1964. The WCF was operated for nearly 7500 hr, and some 510,000 gal of wastes was processed during this period. The overall reduction in the liquid-to-solids volume was about nine. The solids are estimated to occupy a volume of about 7500 cu ft in the existing waste-calciner solids-storage bins.[9] Decontamination of the WCF is in progress.[8,10,11]

Before operation of the WCF with radioactive feed can be resumed, a new solids-storage facility must be constructed.[10] The new facility will consist of seven 12-ft-diameter bins located in a single 44-ft-diameter circular vault. The bins will be cooled by natural air convection, and the vent system will be connected to the existing solids-storage vent system. Six-inch-diameter lines will be installed to permit retrieval of solids from the bins at a future date. Design of this facility has started.[10,11]

During operation of the fluid-bed calciner at the WCF, radioactive fines that are entrained in the off-gas are reduced to a safe level before discharging the off-gas to the atmosphere.[7] A louvered baffle (Fig. IV-4), located in the vapor spacer of the calciner vessel, deflects back to the bed a large portion of the particles that leave the fluid bed. A primary multiple cyclone then removes from the off-gas a major portion of the fines that leave the calciner vessel. Petrie and Black[12] at ICPP have summarized work done on cyclone performance. This work resulted in modifications of the originally installed primary cyclone prior to the start of the recently terminated run with actual plant wastes. The modified cyclone is shown in Fig. IV-5. On the basis of the test results, an inlet gas velocity of 32 ft/sec was provided to each of the nine individual cyclone elements within the multiple cyclone. For calcination processes producing alumina, this inlet velocity results in maximum cyclone collection efficiency and minimum particle attrition and particle breakup within the cyclone. The fines separated by the cyclone are combined with the calciner-vessel product, which is then continuously transported pneumatically to shielded storage bins. The modified multiple cyclone offers the following design features: reliability, low pressure drop, simplicity, and relative ease with which it can be decontaminated.

Conversion to Glasses

Russian work on the fixation of high-level-activity wastes in vitreous glasses and the storage of these glasses was reported (Ref. 13) at the Third Geneva Conference. The process, which has been tested on a pilot-plant scale (Fig. IV-6), comprises the following steps:

1. Precipitating the hydroxides of metal ions from nitric acid wastes. The resulting slurry serves as feed material for the next step.

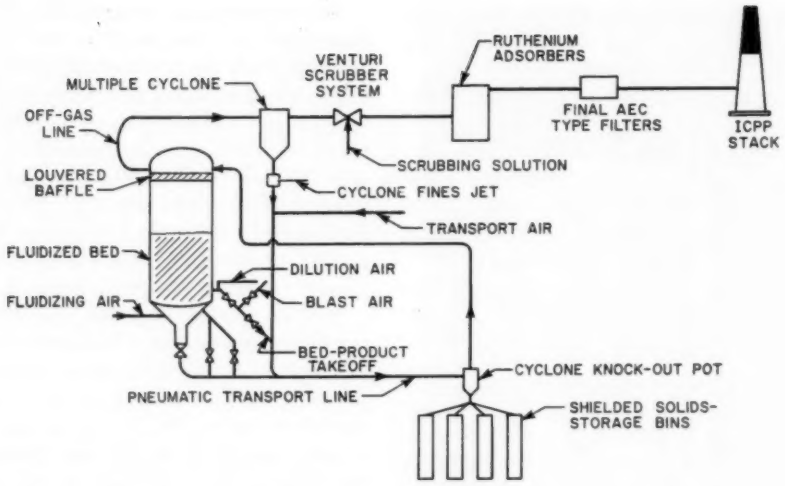


Fig. IV-4 Process flow sheet of the Waste Calcining Facility.[12]

2. Fluid-bed calcining at 700°C to dehydrate and calcine the slurry feed material from the previous step. Sand is used as the fluid-bed material. The calcined waste particles are elutriated from the fluid bed and collected in a cyclone separator.

3. Mixing the calcined product material from the cyclone separator with a natural flux material (ulexite, albite, and others) and carrying out the melting at about 1100°C.

4. Casting the melt into a block.

In a study related to the burial of glass blocks, testing of the radiation stability of vitreous preparations was undertaken. Ionizing radiation destroyed the surface of the glass and increased its solubility in water. This was believed to be caused by the radiation-induced chemical reaction of surface components of the vitreous preparations with air. A sharp lowering of this effect was found with increasing temperature. The change in the surface structure is not appreciable above 1500°C since the gas adsorp-

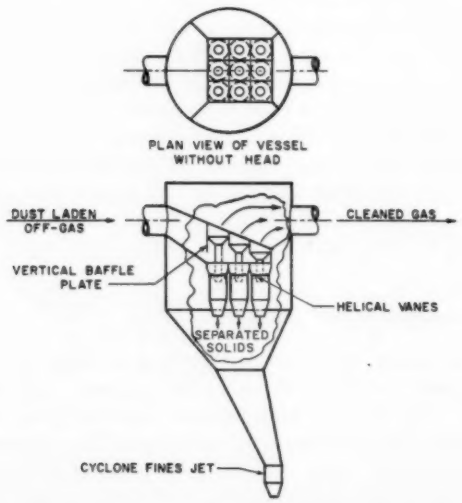
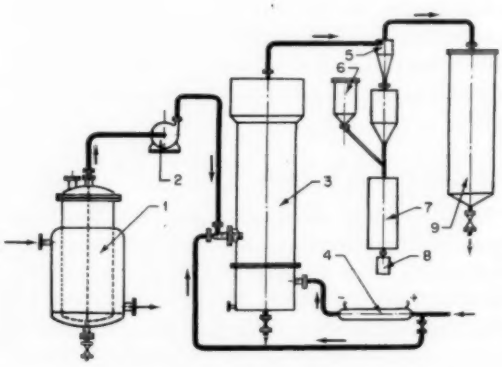


Fig. IV-5 Final modified version of multiple cyclone used in the Waste Calcining Facility.[12] *(Courtesy of Oak Ridge National Laboratory.)*



1, feed tank
2, feed pump
3, fluid-bed calciner
4, steam superheater
5, cyclone separator
6, flux feeder
7, flux melter
8, melt receiver
9, off-gas treatment

Fig. IV-6 Schematic diagram of the pilot plant for the Russian glass-fixation process.[13]

tion on the surface of the preparation decreases and the annealing of radiation defects occurs. Thus it was suggested that the radiation-induced chemical destruction of glass blocks may be prevented by maintaining storage temperatures not lower than 150°C and minimizing air contact with the vitreous preparation.

Various approaches for burial disposal with and without cooling of glass blocks were also investigated. Of the various burial methods studied, two are briefly described here. The first method involves designing the burial area so that the heat evolved from the high-level-activity glass blocks is used to melt a glass-forming mixture, which is charged to the burial area.[3,13] The mixture is a combination of the calcined solids from low-level-activity wastes and glass-forming additives and should have a lower melting point (200 to 300°C lower) than that of the glass block. After cooling, the glass block is contained within a glasslike monolith. The second method involves utilizing the large amount of heat evolved from the high-level-activity glass blocks to heat to about 500°C the surrounding earth in the waste-burial area.[13] This high temperature would serve as a heat barrier and thus prevent groundwater from reaching the glass blocks.

Harwell Glass-Fixation Process

Work at Harwell on a process for incorporating high-level-activity wastes in glass has been summarized in a Third Geneva Conference paper, Ref. 14. [Details of this process were discussed in the Summer 1964 issue of this journal (Ref. 15)]. A simplified process flow sheet is shown in Fig. IV-7. Radioactive nitric acid wastes, together with glass-forming materials, flow into a stainless-steel vessel held at a temperature of 1050°C. Evaporation, denitration, sintering, and glass formation occur steadily during a complete loading cycle. The nitric acid vapors produced are filtered in a second vessel identical with the first. These vapors are further filtered in a similar third vessel before condensation occurs, and radioactive ruthenium is adsorbed on ferric oxide held inside the filter units. The process is maintained at subatmospheric pressure by an air ejector. When the first vessel has been filled, the second vessel is moved into the first position. A fusible link allows the filter to fall to the bottom of the vessel, and the filter and its accumulated dust are incorporated into the next charge of glass. Decontamination factors of 10^8 between feed and condensate and about 10^{10} between feed and effluent air are desirable. However, some relaxation of the former value is possible if the small volume of condensate that forms can be readily recycled to a primary evaporator.

A pilot plant has been operated with 6-in.-diameter vessels. Glass blocks (borosilicate type) have been produced from feed solutions containing added radioactive tracers (^{142}Pr and ^{103}Ru) and up to 1000 curies of mixed-fission-

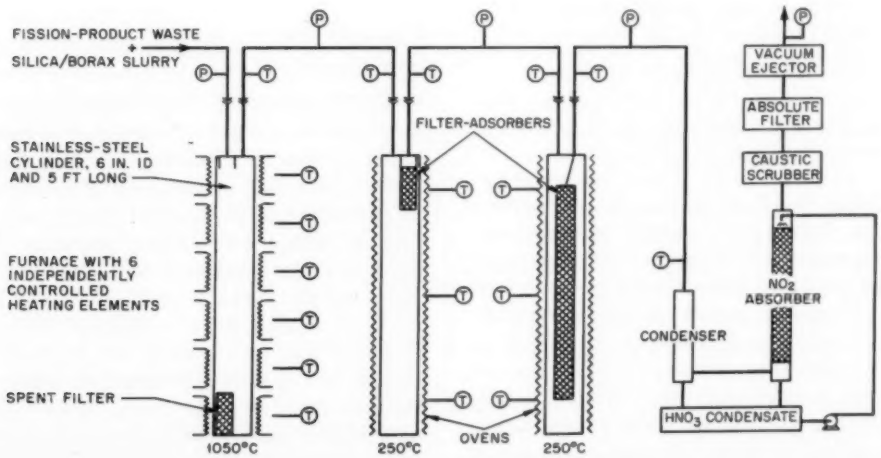


Fig. IV-7 Simplified flow sheet of process for incorporation of fission-product wastes into glass.[14]

product activity. In a run with ^{142}Pr tracer, which is typical of a nonvolatile fission product, the decontamination factor between feed and condensate was greater than 10^6 when filters were used in the second and third vessels. In the runs with mixed-fission-product tracer or ^{103}Ru tracer, the ruthenium behavior was variable. However, effective ruthenium removal is not believed to present a severe technological problem. In two mixed-fission-product runs, ruthenium decontamination factors (ratio of amount of ruthenium in feed to amount of ruthenium in condensate) greater than 10^8 were observed after many hours of operation. However, these high values were not maintained throughout either of the runs, the overall run decontamination factors dropping to 2×10^4 and 8×10^4, respectively, in each run. This reduction in the ruthenium decontamination factor is believed to be associated with an increased pressure drop across the filter-adsorbers because of increased dust loading during the course of the run. Thus the gas velocity through the adsorbers would steadily increase to maintain the subatmospheric pressure in the process vessel. Earlier work[3] had shown ruthenium adsorption to be dependent on superficial gas velocity. By contrast, in the ^{103}Ru tracer runs, the ruthenium decontamination factors were initially low but increased to reasonably high values, which then remained constant for the remainder of the run. In two such runs, for example, decontamination factors of 4.4×10^3 and 1.6×10^5 were achieved. In two runs with feeds containing 55 and 1000 curies of mixed-fission-product activity, overall decontamination factors for beta-gamma activity were 2.1×10^5 and 8.1×10^5, respectively.

Chalk River Ground-Disposal Experiment with Radioactive Glass Blocks

Merritt and Parsons at Chalk River have reported in Ref. 16 the results of a ground-disposal experiment that examined the leaching of radioactivity from glass blocks, each of which contained about 45 curies of mixed-fission-product activity. The function of the soil is to provide permanent radiation shielding and an ion-exchange medium for the anticipated small release. The glass blocks were buried below the water table in sandy permeable soil (10 to 12 ft below ground level). The continuous passage of groundwater would thus effect leaching. The groundwater at the burial site had a *p*H of 6 and a mean temperature of 6°C. It had a total solids content of 30 ppm, of which the main constituents were iron, aluminum, calcium, and silica, and lesser amounts of sodium, potassium, and magnesium. Twenty-five radioactive glass blocks (nepheline syenite*-based[17]) were prepared for the experiment. The blocks were hemispherical (5.5 in. in diameter); each one contained about 45 curies of mixed-fission-product activity, including 23 curies of ^{137}Cs, 20 curies of ^{90}Sr, 2 curies of ^{144}Ce, and 0.2 curie of ^{106}Ru. The total activity for the experiment was about 1100 curies. The blocks were buried in a grid pattern that permitted the free passage of water through the grid and promoted a well-defined track of leached fission products downstream. (Only 22 of the 25 blocks were acceptably positioned for the experiment.) Monitoring of the experiment was carried out over a three-year period. The escape of hazardous radionuclides was within acceptably low limits. For example, the total amount of ^{90}Sr leached in three years from all glass blocks amounted to about 1.1 mc (original total amount of ^{90}Sr present, 440 curies). In a partially water-saturated zone, such a release may be expected to be orders of magnitude lower than the release rates found in this experiment. Thus it was concluded that this method of disposal would be safe, even in water-saturated soil with a low exchange capacity.

Final Disposal Methods

Disposal by Hydraulic Fracturing into Shale

ORNL is continuing its investigation to determine the feasibility of disposing of radioactive liquid wastes into shale or other suitable geologic formations by means of a hydrofracturing technique.[18] In this approach the aqueous waste is first mixed with cement and clay, and then the slurry is pumped at high pressure into the rock strata through a deep, specially constructed hole. When sufficient pressure is exerted, the rock strata are fractured at the bottom of the hole and the waste slurry is distributed in a thin horizontal layer around the hole where the waste hardens. This technique

*Nepheline syenite is a silicate rock used in the glass and ceramic industries.

is being considered for the disposal of the large volumes of intermediate-level-activity wastes that are produced at ORNL.

The construction of an injection plant has been completed at ORNL.[2,19] A view of the completed plant is shown in Fig. IV-8. A series of

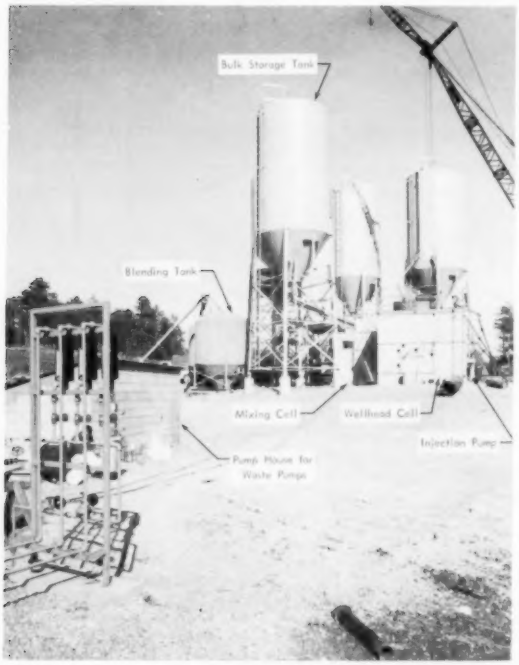


Fig. IV-8 View of completed injection plant for hydrofracturing waste-disposal experiments at ORNL.[2]

five injection tests was made with waste solutions and solid mixes of different compositions into an approximately 1000-ft-deep hole to test the performance of the surface plant and to determine the underground behavior of the grout sheets formed.[20,21] Simulated ORNL waste-evaporator concentrate solutions (10-fold concentration), actual ORNL plant intermediate-level-activity wastes, and mixtures of these two wastes were used as feed materials in these injection tests.

Evaluation of the mixes used in the five injection tests and determination of the underground behavior of the grout sheets will be made when cores of the formation have been recovered. Core drilling is in progress.[22]

In general, the operation of the surface plant was satisfactory. Minor difficulties with various components of the surface plant were corrected as they appeared. The disposal operation became almost routine as experience was being accumulated.

Calcined-Solids Storage in Salt Mines

A field demonstration of the storage of high-level-activity waste solids in salt is being planned for the Carey Salt Company mine in Lyons, Kans.[23] Figure IV-9 is a cutaway drawing of the experimental arrangement in the mine. The objectives of this experiment are to demonstrate equipment and techniques for the safe handling and storing of high-level-activity wastes in a solid form and to study the effects of radiation and heat on the salt.[20] Because calcined waste solids of sufficiently high fission-product heat will not be available in time for this test, spent fuel elements from the Engineering Test Reactor (ETR) at NRTS, Idaho, will be used to simulate the calcined waste. Fourteen ETR fuel elements will be contained in seven canisters. The canned fuel elements will be placed in a circular array of holes in the mine floor; one can will be located in the center, and the other six cans will be located peripherally on 5-ft centers. In addition, an identical array with electric heaters has been located in a separate room and will be operated for control purposes. A similar array of heaters has been placed in a center pillar to obtain information on creep and plastic flow of salt at elevated temperatures. This field experiment is expected to be completed within a two-year period.

Preparation of the Lyons mine for the experiment is in progress.[2,21] Except for the waste-charging shaft facility, renovation of the above-ground facilities has been completed.[25] Construction of the waste-charging shaft (19 in. in diameter by 1000 ft in depth) has been finished. Underground mine work on tunnel clearing of the main access tunnels and ramp building is in progress.[26] Concurrent with the mine clean-up, gauges for measuring plastic flow are being installed along the access tunnels and near the experimental area.[21] The information obtained from these gauges will be used to determine the effect of increased temperature on stability of the mine.

Design of all major pieces of equipment for handling and storing the ETR fuel elements has been completed.[2,21] These equipment items include the following: (1) fuel-element canisters

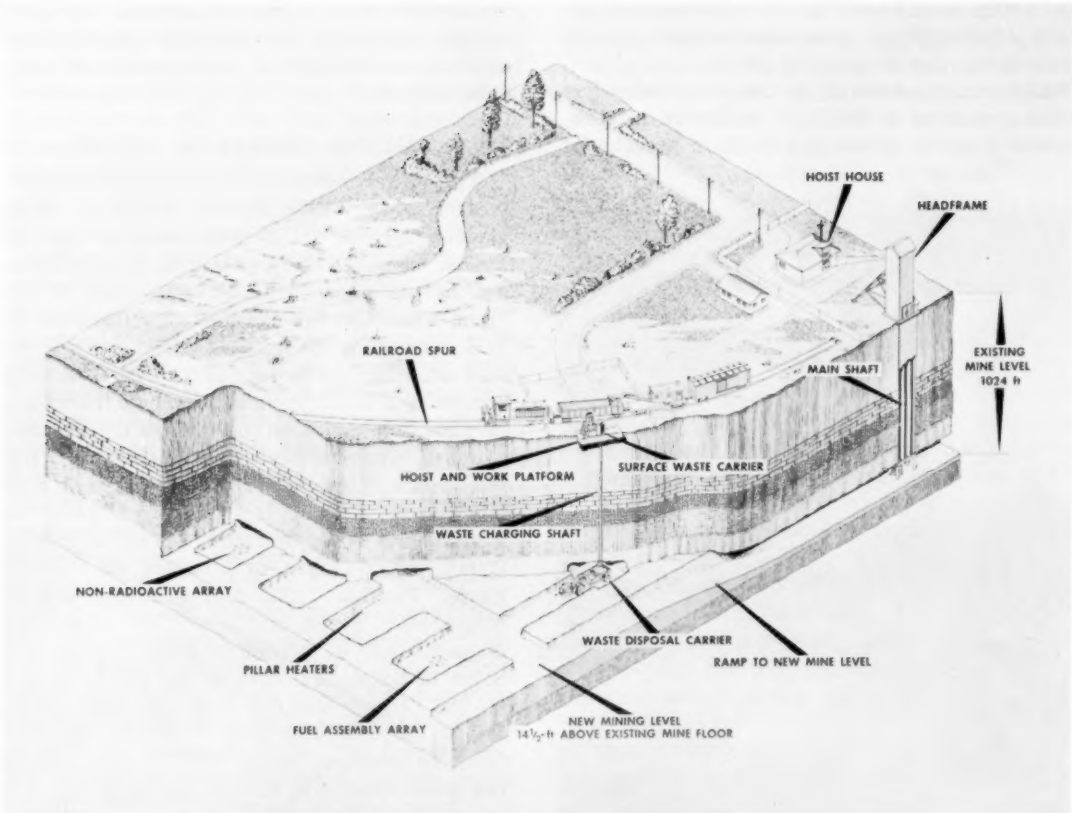


Fig. IV-9 Demonstration of radioactive solids disposal in salt.[24]

designed to hold two ETR fuel elements, (2) hole liner assemblies[23] for preventing contact between the salt and the canisters and ensuring removal of the canister at the end of the experiment, (3) surface shipping carrier for transporting ETR fuel elements between NRTS, Idaho, and Lyons, Kans., and (4) underground transporter for below-surface use in the mine. Procurement of equipment items is in progress.

Fission-Product Recovery

Tomlinson, Judson, and Zahn at Hanford have reported in Ref. 27 on the processes used in the United States for the isolation and purification of various fission products (strontium, cerium, promethium, barium-lanthanum, and technetium). Some of the processes that are available for recovering strontium, cerium, and promethium are shown in Table IV-1, and processes for cesium and technetium are shown in Table IV-2. The authors have described briefly the large-scale fission-product-production activities and have indicated some of the plans that are being implemented to provide increased capability for recovering selected fission products. Pertinent characteristics of three types of intersite shipping containers for fission products are presented.

Raggenbass of the French Commissariat à l'Énergie Atomique has outlined in Ref. 28 the separation processes that have been investigated for the recovery of cesium, strontium, and rare earths from fuel-processing waste solutions. Precipitation and ion-exchange processes were studied for the recovery of ^{137}Cs from uranium fuel and uranium-molybdenum-alloy fuel wastes. The precipitation process utilized phosphotungstic acid; the ion-exchange process used an ion exchanger prepared by precipitating zirconium

Table IV-1 PROCESSES FOR RECOVERING STRONTIUM, CERIUM, AND PROMETHIUM FROM ACID MEDIA[27]

Operation	Method*	Reagent	Status†	Remarks
Sr, Ce, and RE* removal from Purex acid waste	PPT	Sulfate	P	$PbSO_4$ carrier; metathesize with Na_2CO_3
	SE	D2EHPA*	P	Extract at *p*H 4 to 5
Sr separation from Ce and rare earths	PPT	Oxalate	P	
	SE	D2EHPA	P	Selectively strip Sr from solvent
	IX	Cation exchanger	L	Use to purify Sr
Ce separation from rare earths	SE	D2EHPA	D	Selectively strip RE, leaving Ce(IV) in solvent
	PPT	Peroxyacetate	D	Precipitate at *p*H 4
Pm separation from rare earths	SE	TBP	L	Extract with 100% TBP
	SE	D2EHPA	L	
	IX	Cation exchanger	L	Chromatographically elute, using chelating and restraining ions

*PPT denotes precipitation; SE, solvent extraction; IX, ion exchange; D2EHPA, di-2-ethylhexyl phosphoric acid; RE, rare earths, including promethium.

†P denotes extensive use in production activities; D, demonstration in production-plant equipment; L, demonstration in laboratory equipment.

Table IV-2 PROCESSES FOR RECOVERING CESIUM AND TECHNETIUM[27]

Source*	Method†	Reagent	Status‡	Remarks
		Cesium recovery		
Alkaline wastes	IX	Zeolite	P	Elute with NH_4NO_3 or $(NH_4)_2CO_3$
Alkaline wastes	PPT	Nickel ferrocyanide	D	Metathesize with silver
Alkaline wastes	SE	Substituted phenols	L	Strip with dilute HNO_3
Alkaline wastes	SE	Dipicrylamine	L	Strip with dilute HNO_3
Acid wastes	PPT	Aluminum sulfate	P	Fractional crystallization
Acid wastes	PPT	Phosphotungstate	D	Metathesize with NaOH
Acid wastes	SE	BAMBP-D2EHPA§	L	Synergistic effect at *p*H 4-5
Acid wastes	IX	Zeolite	L	Scrub Zr-Nb with oxalate
		Technetium recovery		
Gaseous UF_6	IX	Magnesium fluoride	P	Strip with water
Acid solutions	SE	Tertiary amine	P	Strip with NaOH or Na_2CO_3
Alkaline solutions	IX	Anion exchange	P	Elute with concentrated acid

*Alkaline wastes denote the supernatant solutions, free from precipitated salts, in the stored wastes; acid wastes include the salts of process chemicals and corrosion products.

†PPT denotes precipitation; SE, solvent extraction; IX, ion exchange.

‡P denotes extensive use in production activities; D, demonstration in production-plant equipment; L, demonstration in laboratory equipment.

§BAMBP denotes 4-*sec*-butyl-2-α-methylbenzyl phenol and D2EHPA, di-2-ethylhexyl phosphoric acid.

phosphate in a suspension of ammonium phosphotungstate. Satisfactory recoveries of cesium have been demonstrated by both methods. A solvent-extraction procedure has been examined for the recovery of ^{90}Sr and rare earths from the process wastes of uranium-molybdenum-alloy fuels. The extraction solvent is D2EHPA (di-2-ethylhexyl phosphoric acid) diluted with *n*-dodecane and tributyl phosphate (TBP). Excellent recoveries of rare earths and ^{90}Sr have been achieved.

Workers at the Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium, have reported in Ref. 29 the discovery of a new family of synthetic mineral ion exchangers, ferrocyanide molybdate and ferrocyanide tungstate, which show excellent promise for the recovery of cesium from acid waste solutions. The ion exchangers are prepared by precipitating Na_2MoO_4 or Na_2WO_4 in an acid medium with $H_4Fe(CN)_6$. In column tests with simulated processing waste solutions, the ferrocyanide molybdate ion exchanger demonstrated an extremely high affinity for cesium. The efficiency of cesium separation from a 2*M* nitric acid waste solution is high. A maximum loading of 0.5 meq of cesium per gram of exchanger can be achieved at this acidity. The adsorbed cesium may then be eluted with ammonium salts.

Other Literature

Domish and Hatch at BNL have issued a summary report (Ref. 30) on the development work that was conducted on a rotary-ball kiln

process[31,32] for the calcination of high-level-activity liquid wastes. Reference 30 gives details of the development of a special rotary seal and summarizes results of the extensive corrosion studies that were carried out for the selection of construction materials suitable for service in the calcination of wastes containing both fluorides and nitrates. A pilot-scale plant was constructed and operated continuously for one month. After an analysis and evaluation of the results of this extended run, the decision was made to discontinue further development work on this calcination process. Other calcination processes are believed to be less complicated and more promising than this one.[32]

The International Atomic Energy Agency (IAEA), Vienna, has issued a report (Ref. 33) on the management of low- and medium-level-activity liquid wastes and its relation to total containment. (The treatment and containment of highly radioactive liquid wastes and gaseous wastes were not considered in Ref. 33.) The report is based on a panel discussion held in February 1962 at Vienna. The panel was convened to relate radioactive-waste-management practice to total containment, to determine how closely total containment might be approached using present technology, to assess the effects of research and development work that is under way, and to point out what further technological developments are needed. The experiences and practices for the handling and treatment of low- and medium-level-activity liquid wastes together with the results obtained at these establishments are presented in Ref. 33.

The following paragraphs are notes on a number of Third Geneva Conference papers on waste disposal and related topics.

Belter reviews (Ref. 34) the advances in the treatment and disposal of low- and high-level-activity wastes in the United States and their probable effects on the future of the U. S. nuclear power industry. Engineering evaluation studies, in connection with waste-management operations in a future U. S. nuclear power economy, indicate costs of about 0.03 mill/kw-hr for the treatment and storage of high-level-activity wastes. This cost represents about 1% of the total fuel-cycle cost and substantially less than 1% of the cost of nuclear power in a 4 mill/kw-hr economy. He suggests that waste-management costs will not hinder the development of economical nuclear power.

Highlights of U. S. waste-management experience for 1958 to 1963 are described by Belter in Ref. 35. The experiences of major nuclear facilities on the handling and treatment of their wastes are summarized in the reference. Among the methods discussed are tank storage, land burial, and sea disposal. The costs of radioactive waste management are given. Belter states that U. S. radioactive-waste-management operations have not resulted in any harmful effects on the public, on the environment, or on the natural resources. Extensive and continuous surveillance programs are being carried out to assure that concentrations of radioactive material released to the environment do not exceed internationally accepted health and safety standards.

Experience in the controlled release of low-level-activity liquid wastes to North American surface rivers and lakes is reported by Parker et al. in Ref. 36. Data are included for the government-owned facilities at Chalk River, Hanford, Oak Ridge, and Savannah River and for U. S. nuclear power stations. The fate of the radionuclides released to the environment receives continuous attention and evaluation. It is pointed out in Ref. 36 that, since these installations have controlled their releases of radioactive liquid wastes, the exposure of people from this source has been considerably less than the limits recommended by the International Commission on Radiological Protection (ICRP) and other authoritative bodies.

McBride and coauthors have considered in Ref. 37 the nuclear safety procedures and experience of fuel-processing plants in the United States. In their discussion of confinement of radioactivity, they point out that millions of curies of fission products enter the fuel-processing plants every day. Although the fission products are relatively immobile at the time of receipt, they are in a highly mobile form throughout the rest of the process. Therefore extreme precautions are taken to ensure that no process stream is released to the environment containing sufficient activity to constitute a hazard to important life forms. More than 99.99% of this fission-product activity is in the high-level waste stream that goes to underground storage tanks at the plant site. The remainder may find its way to the environment by any of several routes: discharge of gases to the air through the plant stack; discharge of liquids to the ground as process condensates, cooling

water, or storage-basin overflow; or discharge of solids to the ground through burial of such materials as gloves, cleanup rags, analytical laboratory wastes, and contaminated equipment. Typical data for release of radioactivity from U. S. fuel-processing plants are summarized in Table IV-3.

Table IV-3 ACTIVITY RELEASES TO ENVIRONMENT FROM IRRADIATED-FUEL-PROCESSING PLANTS (REF. 37)

(Data Are Given in Curies)

	1963			1962			1961			1960			1959		
	SRP*	Hanford	ICPP*	SRP*	Hanford	ICPP*	SRP*	Hanford	ICPP*	SRP*	Hanford	ICPP*	SRP*	Hanford	ICPP*
Airborne, via stack	9	139	102	19	102	258	167	255	326	17	350	262	177	296	11,404†
To ground, via seepage	261	37,200	18	227	63,700‡	48	183	8,200	18	466	7,800	4	230	8,700	12
Direct disposal															
To surface water	1			1			3			8			1		
To underground water			6			29			30			32			46

*SRP denotes Savannah River Plant; ICPP, Idaho Chemical Processing Plant.
†Greater than 90% from burst during criticality incident.
‡Increase due to process change, principally ruthenium.

Surrounding each of the fuel-processing plants in the United States is an extensive network of monitoring stations. At none of the sites has the level of any of the monitored isotopes been more than a few percent of the appropriate values in the Radiation Concentration Guide (RCG) for off-site radiation levels.

Two British papers (Refs. 38 and 39) outline the systems used at Windscale for the treatment of radioactive liquid wastes[40] arising from two fuel-processing plants. The handling and processing systems for low-, medium-, and high-level-activity liquid wastes are discussed in the papers. The low-activity wastes are monitored at the processing plant, are neutralized at the waste-treatment plant, and are then batch monitored before discharge to the sea. Treatment of the medium-activity wastes depends on their composition and is by one of the two following techniques: (1) chemical precipitation followed by storage of the sludge and discharge (after monitoring) of the supernatant solution to the sea and (2) evaporation for volume concentration only or for volume concentration and nitric acid recovery. Treatment of the concentrate from the medium-activity evaporator depends on the activity level, and the concentrate is either tank-stored for decay of fission-product activity or sent to the evaporation plant for highly radioactive wastes for further concentration and storage. Overall, these waste-treatment systems have apparently given consistent radioactivity-removal efficiencies and safe containment for the activity arising at the Windscale processing plants.

Processes and facilities for the treatment of solid and low- and medium-level-activity liquid wastes at the French atomic energy centers of Grenoble, Marcoule, and Saclay are described in two papers (Refs. 4 and 41). These papers discuss the effectiveness of these systems and improvements that have been made.

The waste-treatment systems employed at the Atomic Energy Establishment at Trombay, India, for processing the various types of solid and liquid radioactive wastes are described in two papers (Refs. 42 and 43). Currently the wastes arise from reactor operations and production and research facilities. In the future additional wastes will be generated from a fuel-processing plant that is nearing completion. Treatment methods include the following: flocculation and ion exchange, evaporation, incineration, and baling. The high-level-activity liquid wastes from the fuel-processing plant (based on the Purex process) will be evaporated, and the concentrated solution will be stored in underground, stainless-steel-lined concrete tanks.

Richter-Bernburg has considered in Ref. 44 the creation of deep underground cavities in salt formations located in western Europe for the ultimate storage of radioactive liquid wastes. He concludes that salt formations in many places in western Europe are suitable for this application. He considers rock salt (halite) in its natural subsoil position to be truly impermeable to groundwater. He suggests that cavities created in salt formations of the salt-

dome (diapers) type are better for waste storage than in those of the salt-table type.

(Phillip Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Preparation and Properties of Uranium Trioxide

Uranium trioxide is an important intermediate in the commercial production of uranium dioxide and uranium tetrafluoride. The properties of the UO_2 produced by hydrogen reduction of UO_3 and the rate of the reduction reaction are both greatly affected by the structure of the parent UO_3 which, in turn, is dependent upon the conditions and methods used in the preparation of the UO_3. Uranium trioxide is prepared commercially either by calcination of uranyl nitrate solutions in fluid-bed reactors or pot calciners or by thermal decomposition of ammonium diuranate.

Decomposition of Uranyl Nitrate Hexahydrate

Although the thermal decomposition of uranyl nitrate hexahydrate (UNH) is an important step in the production of UO_3, many uncertainties exist in the process performance owing to the lack of information on the decomposition of UNH. Hartland and Nesbitt have studied (Ref. 1) the mechanism of the decomposition reactions under conditions similar to those existing in a fluid-bed plant by decomposing samples of UNH in a hot air stream at temperatures between 100 and 350°C. Rate data obtained at temperatures between 200 and 350°C suggest that the decomposition of UNH proceeds by two first-order reactions with $UO_2(NO_3)_2 \cdot H_2O$ as an intermediate compound:

$$UO_2(NO_3)_2 \cdot 6H_2O \rightarrow UO_2(NO_3)_2 \cdot H_2O + 5H_2O \quad (1)$$

$$UO_2(NO_3)_2 \cdot H_2O \rightarrow UO_3 + 2NO_2 + 0.5O_2 + H_2O \quad (2)$$

The reaction rate for Eq. 1 is much more rapid than the reaction rate for Eq. 2. The authors of Ref. 1 suggest that the rate of chemical reaction is the mechanism controlling the overall rate of decomposition. These conclusions are at variance with those from other work reported in the Spring 1964 issue of *Reactor Fuel Processing*,[2] in which it was suggested that the decomposition of UNH proceeds by a zero-order heterogeneous autocatalytic reaction.

In an investigation of methods for preparing UO_2-dispersed graphite-base fuel, Iwamoto[3] has determined the composition of products formed in the thermal decomposition of UNH in the presence of graphite. The effect of graphite on the nature of the decomposition products is not observed at temperatures below 500°C. In the absence of graphite, UNH decomposes to give UO_3 or U_3O_8 at temperatures from 500 to 800°C, and decomposition in the presence of graphite leads to the formation of lower oxides of uranium (U_3O_8, $UO_{2.25}$, and UO_2). At 800°C, UO_2 was the only product of the decomposition of UNH in graphite.

Hydrates of Uranium Trioxide

When UO_3 produced by spray denitration of uranyl nitrate in a fluidized-bed reactor is reduced by hydrogen, a relatively unreactive grade of UO_2 is the product. An activation procedure based on the conversion of uranium trioxide to hydrated species followed by dehydration and reduction has been developed to produce a reactive form of uranium dioxide. Details of this activation technique were reported in the October 1962 issue of *Reactor Fuel Processing*.[4] The reactivity of UO_3 toward reduction to UO_2 and subsequent hydrofluorination to UF_4 depends on the conditions of hydration and dehydration. High reactivity is favored by hydration under conditions which minimize crystal growth and which lead to the formation of a

dihydrate species rather than a monohydrate species. The UO_3-H_2O system is highly complicated, especially since there are five crystalline polymorphs and an amorphous variety of UO_3, all of which can form hydrates. Wheeler and associates[5] have investigated the UO_3-H_2O system and have observed that UO_3 can form hydrates under a variety of conditions and that five different hydrate species can be identified crystallographically: $UO_3 \cdot 2H_2O$, $UO_3 \cdot 0.5H_2O$, and three forms of $UO_3 \cdot H_2O$. The products of the decomposition of each hydrate species have been identified. Rode and associates[6] have also reported the results of a comprehensive study of UO_3 hydrates. In other work Cordfunke and Debets[7] have reported the existence of a monohydrate species that had not been previously characterized.

The hydration-dehydration technique has been used as a means for varying the surface area of UO_3 powders.[8] In all cases the technique resulted in the lowering of the particle surface area. The surface area of the dehydrated material was primarily governed by the surface area of the initial hydrated oxide. Crystal growth occurs during the hydration step, and this crystal structure is retained after dehydration.

Production of Uranium Tetrafluoride

Uranium tetrafluoride is an important intermediate in the production of both uranium hexafluoride and uranium metal. Uranium tetrafluoride is prepared commercially either by reaction of uranium dioxide with hydrogen fluoride or by reduction of uranium hexafluoride with hydrogen.

At the uranium production plant at LeBouchet, uranium tetrafluoride is produced from UO_3 by a reduction-hydrofluorination process.[9] Instead of using separate reactors for the reduction and hydrofluorination steps, one reactor in two stages accomplishes the same result. Uranium trioxide in the form of flakes enters the top of the two-stage moving-bed reactor and is reduced to UO_2 in a gas stream of cracked ammonia. The UO_2 passes through a conical gas barrier into the lower hydrofluorination stage. Although the UF_4 product from the moving-bed reactor is suitable for direct reduction to metal with calcium, it may contain too much oxygen for magnesium reduction. Therefore a horizontal screw hydrofluorinator is incorporated to ensure complete conversion of UO_2 to UF_4. The product (97 to 99% conversion to UF_4) has been found suitable both for the production of metal by magnesium metal and for the preparation of UF_6 for isotopic enrichment.

Production of UF_4 by Thermal Decomposition of $UF_4 \cdot NH_4F$

Uranium tetrafluoride forms a variety of double salts with alkali and alkaline-earth fluorides which are insoluble in aqueous solutions. Similar insoluble double fluoride salts are formed with ammonium fluoride. A process based on the precipitation of $UF_4 \cdot NH_4F$ from a uranyl nitrate solution and the subsequent thermal decomposition of the double fluoride salt in a fluid-bed reactor to give UF_4 has been demonstrated in a pilot plant designed to produce 100 tons of UF_4 per year.[10,11]

The uranium tetrafluoride–ammonium fluoride double salt $UF_4 \cdot NH_4F$ can be precipitated from a solution of uranyl nitrate $[UO_2(NO_3)_2]$, ammonium fluoride (NH_4F), and formic acid (HCOOH) by the introduction of sulfur dioxide at a solution temperature of 88°C. The overall reaction leading to the formation of $UF_4 \cdot NH_4F$ can be represented by the equation:

$$2UO_2^{2+} + 3SO_2 + 10NH_4F \rightarrow 2UF_4 \cdot NH_4F + 8NH_4^+ + S_2O_6^{2-} + SO_4^{2-}$$

The active reducing agent in this reaction is a complex derived from formic acid which is continuously regenerated by sulfur dioxide. Thus formic acid acts as a catalyst in this operation.

The concentration of formic acid was found to be the most significant rate-determining factor in the precipitation of the double fluoride salt.[10] In practice, however, it was observed that the precipitation of ammonium uranyl fluoride $[(NH_4)_3UO_2F_5]$ at the beginning of the reaction imposed an upper limit on the reagent concentrations. Optimum reagent concentrations for plant operation were determined to be:

Reagent	Concentration, g/liter
Uranium as $UO_2(NO_3)_2$	130–140
Fluoride as NH_4F	50–60
Formic acid	65–70

It was necessary to supply a 5% excess of NH_4F and to provide vigorous agitation during precipitation to achieve high yield of $UF_4 \cdot NH_4F$. The bulk density of the precipitate was found to increase significantly with an increase in the degree of agitation; a product with a bulk density of 2.88 g/cm^3 was generally produced. Achieving a precipitate of high density was particularly significant since the precipitate was subsequently thermally decomposed in a fluid-bed reactor. Operation of fluid-bed equipment generally requires a material of high bulk density to achieve satisfactory fluidization behavior.

Thermal decomposition of $UF_4 \cdot NH_4F$ proceeds by the evolution of NH_4F gas. This operation has been demonstrated on a pilot-plant scale in a 30-in.-diameter Monel fluid-bed reactor.[11] This unit was designed to process, on a batch basis, 1200 lb of $UF_4 \cdot NH_4F$ powder. The bed of powder is supported in the reactor on a woven-metal distributor plate. The off-gas from the reactor is passed through a cyclone to collect entrained particles and then through an ammonium fluoride recovery system. The recovery system is based on the condensation of solid NH_4F by rapid cooling of the off-gas stream below 80°C. The nitrogen fluidizing gas stream is filtered through a series of bag filters and then is recycled to the fluid-bed reactor.

The conversion of $UF_4 \cdot NH_4F$ to UF_4 is accomplished by heating the bed, fluidized with nitrogen at 20 cfm, to 315°C, at which point decomposition commences. The decomposition actually proceeds in three stages over a 9-hr period. In the first stage the bed temperature is slowly increased from 315 to 330°C in a 3-hr period during which 60% of the NH_4F is removed. Thereafter the rate of NH_4F evolution decreases markedly, and the result is a rapid increase in the bed temperature to 420°C. The second stage of the decomposition commences at 420°C, and virtually all of the remaining NH_4F is removed during a 2-hr period at 420 to 430°C. The remaining traces of NH_4F are volatilized in 1½ hr at 460°C in the third stage of the decomposition. The final UF_4 product contains less than 20 ppm nitrogen as NH_4F. No UO_2F_2 has been detected in the UF_4. Approximately 0.5 wt.% U_3O_8, probably formed by reaction of the UF_4 with moisture introduced in the $UF_4 \cdot NH_4F$ feed material, has been found in the product. The bulk density of the UF_4 product was approximately 2.8 g/cm^3. Most of the product was particles with diameters of 28 to 53 μ. Dust losses beyond the cyclone were 2.5% of the material charged to the fluid-bed reactor.

Reduction of Uranium Hexafluoride

A method for converting UF_6 to UF_4 by high-pressure reaction of liquid UF_6 with hydrogen at 400°C has been developed in France[12] for processing highly enriched uranium. The major problem encountered in developing a method for reducing UF_6 to UF_4 was the deposition of UF_4 on the walls of the process vessel. Adhesion of UF_4 to the walls was prevented by introducing the UF_6 in the form of fine, liquid droplets under high pressure (80 bars) into an atmosphere of excess hydrogen at 400°C and 20 bars. The reaction between the UF_6 droplets and hydrogen takes place instantaneously without contact with the walls of the reactor. The UF_4 product precipitates as a fine powder and is collected in a receiver at the bottom of the reactor. The product has a bulk density of approximately 2 g/cm^3. The hydrogen fluoride by-product and excess hydrogen are periodically expelled from the pressure vessel to a waste-disposal system.

The pressure reaction vessel is constructed of a nickel tube 80 mm in diameter and 1.8 mm high. The product receiver is 120 mm in diameter and 0.3 m high. Uranium hexafluoride is injected to the reactor under pressure by means of a diaphragm pump. The apparatus is designed to handle 3-kg batches of enriched uranium.

Production and Properties of Uranium Carbide

Interest in using the carbides of uranium as nuclear fuels has grown considerably within the past few years and has stimulated research and development work in many countries. More effort has been devoted to the development of carbide fuels for fast reactors than for thermal reactors since the high thermal conductivity of carbides can best be exploited in reactors of very high power rating. Since a fast reactor should preferably use plutonium as the source of fissile atoms, widespread interest has developed in evaluating (UPu)C as a fuel material.

Results of recent efforts in the development of uranium carbide fuels for power reactors were reviewed in a paper[13] presented at the Third Geneva Conference. A review[14] of British work leading to an evaluation of the monocarbides of uranium and uranium-plutonium as reactor fuels was presented at the same conference.

Reference 15 contains the proceedings of a symposium on carbides in the nuclear energy field held at Harwell in 1963. The papers presented at the symposium covered two broad areas of interest: (1) physical and chemical properties of carbides and (2) preparation, fabrication, and irradiation behavior of carbide fuel materials. Although much of the information presented in the proceedings has been covered in previous issues of *Reactor Fuel Processing*, or is beyond the scope of this review, some recent developments are described separately in this section.

Methods for the Preparation of Uranium Carbide

Among the most promising methods for preparing uranium monocarbides is the reaction between uranium dioxide and elemental carbon at high temperatures. Studies have been made of this reaction in vacuum over the temperature range 1250 to 2200°C. The rate of reaction is first order with respect to UO_2. It has been found[14] that: (1) loose powders react at higher rates than pelleted reactants; (2) the rate of reaction of oxide and carbon is, for pelleted reactants, virtually independent of the particle size of the individual reactants over a considerable size range; and (3) very coarse particles of oxide (>100 μ) react very slowly with carbon. Thus thorough mixing of the reactants is important to avoid large agglomerates of UO_2. In practice it is difficult to avoid some compaction of the reactants, and therefore it is necessary to avoid the use of deep beds of material from which escape of carbon monoxide is difficult.

It is desirable to remove the CO by-product in an inert-gas stream to avoid the use of high vacuum and to render the UO_2-C process more amenable to continuous operation. Harrison and Isaacs[15a] have prepared UC by the reaction of compacted mixtures of oxide and carbon at 1500 to 1600°C in a flowing argon stream. The reaction proceeded smoothly to give products in which the carbon content was regulated to ±0.05 wt.% and in which the oxygen content was below 0.3 wt.%. In other work Fletcher, Hyde, and Landsman[15b] have investigated the application of fluidization techniques to the preparation of UC by reaction of UO_2 with carbon. The process was demonstrated on a small scale using batch operation. Spheroids of UO_2-C mixtures having a particle size of −30 +50 mesh were fluidized in a stream of argon at 1500 to 1600°C. The fluid-bed reactor consisted of a $\frac{3}{4}$-in.-diameter graphite vessel contained within a silica envelope. The reactor was inductively heated by a radio-frequency generator. Preliminary results indicated that complete conversion to UC was accomplished in 3 hr and that the final product contained less than 0.1 wt.% oxygen.

Other methods under study for preparing uranium monocarbide involve the carbothermic reduction[15c] of U_3O_8 and the reaction of propane with finely divided uranium metal.[15d] The preparation of UC by reaction hot pressing of UO_2-C mixtures is discussed in Ref. 15*e*. Uranium monocarbide compacts of 90% of the theoretical density have been prepared by a two-step process: (1) reaction of a UO_2-C mixture in a tungsten foil-lined graphite crucible for 30 min at 1800°C and 0.25-tsi pressure and (2) compaction of the product at 1700°C and 2-tsi pressure for 30 min.

The possibility of synthesizing uranium monocarbide and other refractory compounds of interest as refractory fuels from liquid-metal solutions is currently being investigated at Argonne National Laboratory (ANL).[16,17] The process involves the following steps: (1) dissolution of metallic uranium in a zinc solution containing 14 to 18 wt.% magnesium; (2) addition of degassed, activated charcoal at about stoichiometric quantities to form UC; (3) reaction of the constituents with stirring for 8 to 12 hr at 800°C; (4) a phase separation to remove the bulk of the supernatant liquid metal (Zn-Mg) from the precipitated UC; and (5) vacuum distillation to remove the residual magnesium and zinc from the UC product. The UC prepared by this method has good pressing and sintering properties. Current objectives have been to produce carbide material on a 500- or 1000-g scale with a carbon content near the theoretical value of 4.8 wt.% and as low an oxygen content as possible. Initial tests[16] on a 500-g scale resulted in products containing greater than 0.3 wt.% oxygen. The major source of oxygen con-

tamination was determined to be the activated charcoal, which contributed about 75% of the total oxygen in the starting materials. Efficient degassing of the charcoal has resulted in a significant lowering of the oxygen content of the UC product.[17] Heating activated charcoal to 850°C under continuous evacuation has produced a charcoal product containing 2 wt.% oxygen. It is expected that, by proper handling of materials in an inert atmosphere, a UC product containing less than 0.2 wt.% oxygen can be produced by the liquid-metal-reduction technique.

Sintering Properties of Uranium Carbide

Of the several methods available for the fabrication of carbides into fuel shapes, sintering is particularly suited to the manufacture of cylindrical pieces of 80 to 97% of the theoretical density since the operation can be performed in a continuous manner in geometrically safe equipment. Two factors that affect markedly the sintering behavior of uranium carbide are particle size and oxidation. McLaren, Regan, and Hedger[15f] have observed that UC powder containing a small amount of free carbon will sinter readily to densities greater than 13.0 g/cm^3 at temperatures of approximately 1500°C, provided that the carbide is milled to a fine particle size prior to sintering and that all operations are conducted in a high-purity inert atmosphere. In a study of the sintering behavior of $(U_{0.85}Pu_{0.15})C$, prepared by the reduction of the oxides with carbon, Harrison and associates[15g] observed that the mixed carbide can be sintered to greater than 95% of the theoretical density in an argon atmosphere at 1500 to 1600°C. These results were achieved by reducing the mean particle diameter to about 2 μ and by protecting the powders from oxidation before and during sintering. Sintering aids such as nickel are not necessary for sintering under these conditions. It was observed,[15g] from the sintering behavior of carbide derived from the carbon reduction of the oxide, that oxygen combined as an oxycarbide ($UC_{1-x}O_x$) does not interfere appreciably with sintering. Apparently the poor sintering behavior of powders containing greater than 0.5 wt.% oxygen is due to the metal oxide interfering with the physical processes of shrinkage before reaction of the oxide with the carbide has occurred to convert the oxygen to an oxycarbide phase and CO. In less-oxidized powders the carbide-oxide reaction may remove the oxide before it interferes with the sintering process; thus densification is not impeded.

Taylor, McMurtry, and Anderson[15h] have observed that the use of small amounts of nickel as a sintering aid greatly facilitates the achievement of high-density pellets of uranium monocarbide. The addition of 0.1 to 0.2 wt.% nickel made it possible to obtain densities 95% of theoretical even with considerable variation in powder characteristics and sintering conditions. In the sintering of uranium-plutonium carbides containing greater than 25 wt.% plutonium, sintered densities greater than 97% of the theoretical density can be achieved without the use of a nickel sintering aid.[15i] However, at lower plutonium concentrations in the mixed carbide, the addition of nickel is required to achieve densities greater than 95% of the theoretical density.[15i]

Hammond and Adamson[15j] have developed a method for the fabrication of uranium monocarbide with UAl_2 as a sintering aid. By sintering UC with 5 to 10 wt.% UAl_2 in a vacuum at 1350 to 1400°C, they obtained single-phase uranium monocarbide bodies with densities in excess of 97% of the theoretical density. The aluminum of the UAl_2 is volatilized during sintering, and the uranium from this compound combines with carbon from the graphite containment crucible. Poor aluminum removal and poor densification of the UC resulted from using a UC charge containing extra carbon to provide the amount necessary to combine with the uranium in the UAl_2 sintering aid. The sintering process occurs in three stages: (1) substantial shrinkage occurs by a process activated by aluminum vapor, (2) further consolidation occurs by the presence of a liquid phase in which uranium carbide appears to be soluble, and (3) solid-state sintering is completed by the reaction between free uranium metal and the graphite crucible.

Properties of Uranium Carbide

The preparation of completely single-phase UC is a difficult problem; the slightest deviation from the stoichiometric ratio results in the formation of a second phase, either uranium metal or a higher carbide. The problem is further complicated by the presence of oxygen and

nitrogen, which replace carbon to form solid solutions of the type MC-MN-MO. Anselin and associates have reported in Ref. 15*k* the results of a comprehensive study on the system (UPu)(CNO) and have applied the results to the behavior of uranium carbide during sintering processes. Carbide powders used for sintering are unavoidably contaminated with oxygen to the extent of 1000 to 3000 ppm, which is equivalent to 1.6 to 4.8 mole % UO in "pure" carbides. Consequently in practice the proportions of carbon, nitrogen, and oxygen cannot be rigorously adjusted as required to obtain a single-phase carbide. Excess UO_2 will be consumed during sintering according to Eqs. 1 and 2.

At 1400°C:

$$3UC + UO_2 \rightarrow U_2C_3 + 2UO_{(soln.)} \quad (1)$$

At 1600°C:

$$UC + 2UO_2 \rightarrow 3UO_{(soln.)} + CO \quad (2)$$

For the normal sintering conditions for pure carbides, with a temperature of 1400 to 1600°C and the work done under vacuum, Eq. 1 proceeds more rapidly than Eq. 2, and therefore the resultant carbides are two phase.

Data have been reported on the behavior of carbides in hydrogen and oxygen atmospheres (Ref. 15*l*) and on the solubility of oxygen (Refs. 15*m* and 15*n*) and nitrogen (Ref. 15*n*) in uranium monocarbide. The results of a study on the formation of $UC_{1-x}O_x$ by the reaction of UC and UO_2 or UC_2 and UO_2 at 1200 to 1750°C have been reported by Namba, Imoto, and Sano in Ref. 18.

Thorium

The present position of thorium in the field of power reactors is in the nature of a reserve material. However, considerable technology on thorium chemistry and metallurgy is already available to meet any future production demands. Bril and Krumholz have reviewed in Ref. 19 the recent developments in methods for processing thorium ores, particularly monazite, to nuclear-grade thorium oxide. Reference 19 also gives details of current Brazilian work in the pilot-plant production of ThO_2 from monazite. Recent developments in processing Australian ores have been described by Wylie and Pilkington (Ref. 20).

Production of Thorium Dioxide Powders

Two papers (Refs. 21 and 22) presented at the Third Geneva Conference describe processes based on sol-gel technology for the preparation of dense spheres of thoria or urania-thoria suitable for use in dispersion fuels. Both processes are similar to the sol-gel process developed at Oak Ridge National Laboratory and described in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[23] Hermans and Slooten[21] have applied the sol-gel process to the production of 5.5-μ-diameter thoria spheres. The first step of the process involves the preparation of a sol of hydrated ThO_2 by rapidly mixing a thorium nitrate solution with aqueous ammonia. The sol is dispersed and emulsified by spraying the sol solution into carbon tetrachloride. Individual sol particles are solidified to a gel in a solution of CCl_4 and toluene made alkaline with ammonia. After dehydration the gel spheres are washed, dried, and then fired at 1100°C to a high-density material.

Cogliati and associates[22] have investigated methods for removing nitrate anions from colloidal solutions of thorium hydroxide sols during the gellation step. Two satisfactory methods of producing gels with nitrate-to-metal molar ratios of less than 0.05 are: (1) the use of diluted gaseous ammonia to produce thoria gel, followed by washing the gel with water to remove ammonium nitrate, and (2) the use of aliphatic amines diluted with carbon tetrachloride to extract nitrate as nitric acid from the thoria gel.

Dense thoria bodies can be prepared by sintering thoria powder, and the final density of the sintered bodies is greatly influenced by the method of preparation and by the thermal history of the thoria powder.[24,25] The powder characteristics that lead to high sintered density are small crystallite size and high surface area. These properties enhance densification rate, and appreciably high densities can be attained even at low sintering temperatures. For high-surface-area powders, the temperatures required for nucleation and grain growth may be above those temperatures required for attainment of maximum densification.[25] Therefore the sintering cycle should be so pro-

grammed that high density can be attained in the initial step; and grain development, if desired, can be attained in the second step by continuation of the heat-treatment.

Production of Thorium Tetrachloride and Reduction to Metal

Workers at Ames Laboratory[26] and at the U. S. Bureau of Mines[27] have developed processes for producing high-purity thorium metal by the reduction of thorium tetrachloride with magnesium[26] or sodium.[27] Since the objective of the process-development work was primarily the preparation of low-oxygen-content metal, considerable emphasis was placed on developing methods for the production of pure thorium tetrachloride from thorium oxide. Thorium dioxide loses its chemical reactivity to chlorinating agents if the oxide is heated to temperatures in excess of 650°C prior to chlorination.[27] At the Bureau of Mines,[27] thoria is prepared by the thermal decomposition of thorium oxalate in a packed bed at 500°C while passing a mixture of helium and a gaseous chlorinating agent through the charge. The chlorinating agent maintains a porous stable-oxide bed during decomposition by creating a skeleton framework of thorium chloride to support the thorium oxide powder. A porous bed of oxide is needed for complete conversion to thorium tetrachloride in subsequent operations. Of several chlorinating agents investigated, the use of phosgene at 500 to 575°C gave the highest conversion to $ThCl_4$ in the shortest processing time.[27] As discussed in Ref. 26, preparation of $ThCl_4$ by the reaction of chlorine with ThO_2 in the presence of carbon has also been employed successfully.

Since crude $ThCl_4$ from the chlorinators contains a substantial quantity (up to 7 wt.%) of nonvolatile impurities, the material must be purified prior to reduction to metal. High-purity $ThCl_4$ can be prepared by sublimation[26] or by filtering molten chloride at 900°C through molybdenum wool supported on a fritted Inconel disk.[27] The latter procedure was effective in removing up to 98% of the solid impurities.

The reduction of $ThCl_4$ by magnesium is based on the formation of a thorium–20 wt.% magnesium alloy.[26] Thorium tetrachloride was mixed with sufficient magnesium to reduce $ThCl_4$ and to form the alloy. Reductions were made by heating the charge (4.4 kg of $ThCl_4$ and 1.25 kg of magnesium) in a tantalum crucible under an inert atmosphere for 1 hr at 965°C and for 20 min at 1025°C. The crucible was cooled to room temperature, and the $MgCl_2$ slag was removed from the alloy. An average of 3.2 kg of thorium–20 wt.% magnesium alloy was obtained, which corresponds to 94% yield of thorium metal. The alloy was crushed and heated under a prescribed schedule to 920°C in vacuum to remove the magnesium and residual chlorides. A stepwise heating cycle was used during the magnesium-removal operation to avoid melting of the alloy. The final thorium sponge was consolidated by nonconsumable arc melting and was purified by electron-beam melting.

The reduction of $ThCl_4$ by sodium was conducted in a titanium crucible under an argon atmosphere.[27] Molten sodium (30% excess) was poured into the crucible and was allowed to solidify. The crucible was then filled with solid $ThCl_4$. The reaction was initiated at 550 to 600°C, and, after the initial exothermic reaction was completed, the furnace temperature was increased to 950°C and held for 6 hr to complete the reaction. By-product salts and excess sodium were removed from the thorium sponge by vacuum distillation at 950 to 1000°C. The sponge was consolidated to solid ingots by arc melting. Oxygen content of the final metal was between 700 and 1400 ppm. (J. Barghusen)

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Section

VI

Reactor Fuel Processing

Safety in Chemical Processing

Criticality Incident in Scrap-Recovery Plant

On July 24, 1964, a criticality incident occurred at the AEC-licensed plant of the United Nuclear Corporation (UNC) at Wood River Junction, R. I. The incident caused fatal injuries to one employee, and two other employees received moderately high radiation exposures in succeeding events.

Description of Operations

The Wood River Junction plant consists of a single building and is designed to recover enriched uranium from wastes and scrap materials generated in fuel-fabrication plants. The recovery process involves three principal operations: (1) feed preparation for solvent extraction, (2) separation of uranium from other materials in the wastes and scrap by solvent extraction, and (3) finishing operations in which the uranium is converted to solid uranium dioxide, which is the final product.

At the time of the incident, the plant had been exclusively processing aqueous wastes generated from operations in which fuel materials (uranium-alloy plates) are bathed for cleansing and degreasing prior to cladding or bonding. This waste, called pickle liquor, contains low concentrations of enriched uranium and other metals. After the acidity is adjusted, uranium as uranyl nitrate is recovered by solvent extraction with tributyl phosphate (TBP) diluted with kerosene in a battery of critically safe pulse columns. Uranium is stripped from the solvent into a low-acid aqueous product which is then washed with trichloroethane (TCE) to remove traces of entrained solvent. The TCE is washed with a dilute sodium carbonate solution prior to reuse. The sodium carbonate solution is prepared in a small tank in which the criticality incident occurred.

As the first step of the finishing operations, the aqueous product from the solvent-extraction operation is concentrated in a critically safe evaporator to approximately 100 g/liter. Ammonium diuranate is precipitated from the concentrated solution in critically safe vessels. The precipitate is filtered, dried, and reduced to UO_2 in a furnace. The UO_2 product is then crushed, blended, and packaged for shipment.

Criticality control was based on limitations of one or more of the following variables: volume, geometry, mass, and concentration. Detailed operating procedures included special nuclear safety requirements of the individual processes, such as limitations of batch size and concentration. In some processing tanks normal criticality-control methods were supplemented by including Raschig rings of borosilicate glass where solution concentrations were not expected to exceed 5 g of ^{235}U per liter, but where the nominally safe 5-in. diameter could not be met. Interim product storage was in 5-in.-diameter plastic bottles of 11-liter capacity. These bottles were normally stored in birdcage carts that provided a minimum of 2 ft between bottles.

Description of the Incident

The descriptions reported here of the incident at the Wood River Junction plant of UNC are based on the unpublished findings of a committee formed specifically to investigate and review the event.[1]

OPERATIONS PRIOR TO THE INCIDENT

The Wood River Junction plant had been in operation for only a few months before the

accident occurred. The stripping column had not functioned as well as planned, and more than normal quantities of entrained uranium-bearing solvent were carried through to the TCE. The TCE thus had to be treated to remove uranium more frequently than had been planned. No detailed procedure for this operation had been written; however, a method was devised which involved mixing the TCE with a sodium carbonate solution in an 11-liter bottle and manually agitating the mixture. Since this practice was slow and laborious, an operator proposed to his supervisor that cleaning of TCE could be done more efficiently in the stirrer-equipped sodium carbonate preparation tank. The supervisor concurred with the proposal but stipulated that the uranium concentration of the TCE so treated must be kept below 800 ppm (a safe concentration). Details of this process modification, however, were not communicated to all supervisors or to the plant superintendent.

On July 23, 1964, the day prior to the accident, operating difficulties were experienced with the evaporator used to concentrate the uranium solution prior to uranium precipitation. In correcting this situation, the operators collected two 11-liter bottles of concentrated uranyl nitrate solution. These bottles were labeled "Bottle X, Concentrated Liquor from the Evaporator," and "Bottle Y, Concentrated Liquor from the Evaporator." Although the use of this type of label designation was a violation of established plant procedure, the role that labeling practices played in contributing to the accident has not been definitely established. It is clear that this was the first instance in which concentrated fissionable material was stored in the plant in such bottles. These bottles were stored on isolated carts and were secured by ropes and stanchions.

DESCRIPTION OF THE INCIDENT AND SUCCEEDING EVENTS

At about 6:06 p.m. on July 24, 1964, the operator who was assigned to the extraction-column area poured the contents of "Bottle Y, Concentrated Liquor from the Evaporator," into the sodium carbonate makeup tank that contained 41 liters of 0.54*M* sodium carbonate solution. The tank was an 18-in.-diameter open-top tank (26-in.-deep, dished bottom) constructed of $\frac{1}{8}$-in.-thick stainless steel. This tank had never been meant for use with fissionable material. When approximately 10 liters of the concentrated uranyl nitrate solution had been added to the makeup tank, a nuclear chain reaction occurred, accompanied by a bluish-white light. The excursion caused about 20% of the liquid to eject from the tank. The agitator was on at the time the excursion occurred. The victim fell to the floor; then he rose and immediately ran from the building. He had received an estimated exposure of about 8000 rem. This exposure included 700 rem of gamma radiation and a neutron dose of 2000 to 4800 rads. The operator died 49 hr later in a hospital.

Apparently the loss of fluid (not necessarily of the average composition of the contents of the tank) was such that the vortex and small bubbles from agitation were sufficient to maintain a subcritical state. About 1.75 hr later the contents of the tank were drained into 4-liter bottles. The two men who performed this operation received radiation exposures of about 50 rem each. It is most likely that this exposure resulted from a second nuclear excursion that occurred when the agitator was momentarily turned off while the tank was being drained. No visible evidence of the second excursion was reported, and the solution did not feel warm while being drained.

According to radiochemical analyses of the material from the tank, the total number of fissions was 1.2 to 1.3×10^{17}. The violence of the first event suggests a single fission spike, whereas the second excursion most likely was a sequence of small bursts.

Decontamination of the plant was completed about three weeks after the accident. No plant equipment required replacement. On Nov. 25, 1964, the Wood River Junction fuel-recovery plant received AEC permission to reopen the facility.[2]

Conclusions and Recommendations

The committee that reviewed the incident made a number of recommendations, both explicit and implicit. It was implied that reviews of process difficulties by management and technical personnel and formulation of approved changes in procedure to deal with such difficulties should be frequent.

In the opinion of the committee, control of and access to fissionable material must be commensurate with the hazards involved. It is suggested that day-to-day surveillance of opera-

tions by personnel informed on criticality rules, supplemented by periodic audit of fissionable material, is necessary in operations of this type. In plants where several forms of concentrations of fissionable material exist, there is always a danger of confusion of material. Identification practices must be clear, unambiguous, and reliable.

Indoctrination of plant personnel in operating procedures and safety practices must be emphasized. Training and procedures should provide for coping with process abnormalities. Mechanisms should exist whereby modifications of written procedures can be made after appropriate review. Furthermore, training in nuclear plants should be recognized as being needed on a continuous basis and should emphasize the need for adherence to approved procedures.

The committee also made several suggestions regarding the procedures following a criticality accident. A system that has undergone a criticality accident should be left undisturbed until competent review has produced a plan for the situation. Reentry to the immediate area of the accident prior to this time is warranted only if it is believed necessary to save human life. If there is reentry for this reason, every effort should be made to ascertain the pertinent facts, and, for this reason, portable high-level radiation instruments should be maintained as emergency equipment.

Anion-Exchange Resin Fire

In two recent issues of *Reactor Fuel Processing*,[3,4] details were reported of three incidents involving fires and the venting of overpressured plutonium anion-exchange contactors. It is evident that the maximum safe operating temperature for plutonium anion-exchange systems is substantially lower than previously thought. Nitrate-loaded resin, flooded with liquid, is capable of violent decomposition. A fire that involved anion-exchange resin in neptunium service is described in Ref. 5. A description of this incident is presented here to provide additional information on the hazards associated with the use of anion-exchange resins.

On Oct. 1, 1964, a fire occurred at the Savannah River Plant[5] which involved an anion-exchange column used for the recovery of neptunium from Purex high-activity waste. The entire recovery facility is located in a Hot Canyon, and all operations are performed remotely. An accumulation of solids, which included various chemicals used for column-feed adjustment, high-activity waste concentrate, and organic material from degraded nitrated anion resin, ignited and burned for a short duration. The most likely cause was spontaneous ignition of the mass of accumulated solids by chemical reaction and self-heating as a result of the high concentration of fission products, accelerated perhaps by spillage of 60% nitric acid. The Hot Canyon fire spray system was used to extinguish the fire.

Investigation of the incident revealed that remote repair work was in progress to remove a plug in the anion-exchange-column piping. The column had been emptied of resin, and flushing of the column and associated piping had been under way for several shifts using water and 60% nitric acid. During this operation, spillage of various materials had accumulated around the column. Just prior to the fire, a small leak (~0.5 gal) of 60% nitric acid occurred in the line supplying chemical feed to the column.

The incident was first observed as a white vapor emerging from the base of the column. Immediately flames 2 to 3 ft high were visible. The fire was extinguished by water spray. As a result of the fire, airborne contamination collected on the Hot Canyon crane, and water damaged the electrical motors on the anion-exchange-column agitator and the column-feed-tank agitator. The total damage to equipment, plus the cost to decontaminate the crane, is estimated to be $21,000.

Since the fire occurred in an inaccessible location that can be examined only by the periscope on the crane, the exact cause of the fire has not been determined. It is known, however, that the nitrate form of the anion-exchange resin is flammable when dry. It is certain that the fire did not occur in the column since operations prior to the fire had removed all the resin from the column and had left the column filled with 60% nitric acid. The temperature of the column did not exceed 35°C before or during the fire.

Future installations of anion exchangers will be equipped with a spray system for flushing

external surfaces of the column assembly to prevent recurrence of similar incidents. Dilute sodium hydroxide solutions will be used for flushing and for removing spilled resin to the Hot Canyon sump. Other anion exchangers now in service using nitrated anion resin will be reviewed to determine the feasibility of providing means for flushing the external surfaces of the column and support frames.

(J. J. Barghusen and A. A. Jonke)

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Section

VII

Reactor Fuel Processing

Fuel-Processing Papers from the Third Geneva Conference

Of the papers given at the Third Geneva Conference, some have been reviewed in the preceding issue and some in this issue of *Reactor Fuel Processing*. Since much of the information presented at Geneva has already been reported in *Reactor Fuel Processing*, not all of the papers will be discussed in this Review. To bring all pertinent papers on reactor fuel processing to the attention of our readers, we have listed the Geneva papers on this subject in Refs. 1 to 76. Also listed (Refs. 77 to 81) are other Geneva papers that contain some material related to fuel processing. The reader is also directed to articles reviewing selected Geneva papers on fuel processing (Ref. 82) and waste management (Ref. 83). All Geneva papers that were available were abstracted and indexed in two issues of *Nuclear Science Abstracts* (Refs. 84 and 85).

Copies of the 1964 Geneva papers may be obtained from the following sources:

1. Copies of all papers may be purchased from the European Office of the United Nations for two Swiss francs ($0.46) per paper plus postage. Address: European Office of the United Nations, Palais des Nations, Geneva, Switzerland, Attention: R. Furstenberg, Chief, Distribution Service, Documents Division.

2. When U.N. stocks are exhausted, reproduced copies of all papers may be purchased from the IAEA in Vienna at a price of $1.50 per paper. Address: International Atomic Energy Agency, Kaerntnerring 11, Vienna I, Austria.

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4. The American Nuclear Society will provide Xerox copies of all papers at $0.25 per page. Address: American Nuclear Society, 244 East Ogden Ave., Hinsdale, Illinois 60521.

5. The U. S. Atomic Energy Commission (AEC), Division of Technical Information Extension, Oak Ridge, Tennessee 37831, has produced micronegatives of all Geneva papers. Complete sets of duplicate negatives were distributed to the AEC, other government agencies, and their contractors; sets of U. S. papers only were distributed to AEC depository libraries.

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